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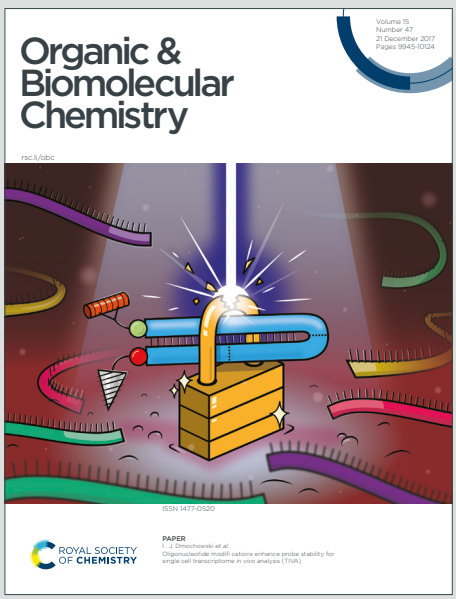

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View Article Online
DOI: 10.1039/C9OB02457C

Organic & Biomolecular Chemistry

PAPER

Bronsted Acid/Visible-Light-Promoted Markovnikov Hydroamination of Vinylarenes with Arylamines†

Received 00th January 201x,
Accepted 00th January 201x

DOI: 10.1039/x0xx00000x

www.rsc.org/

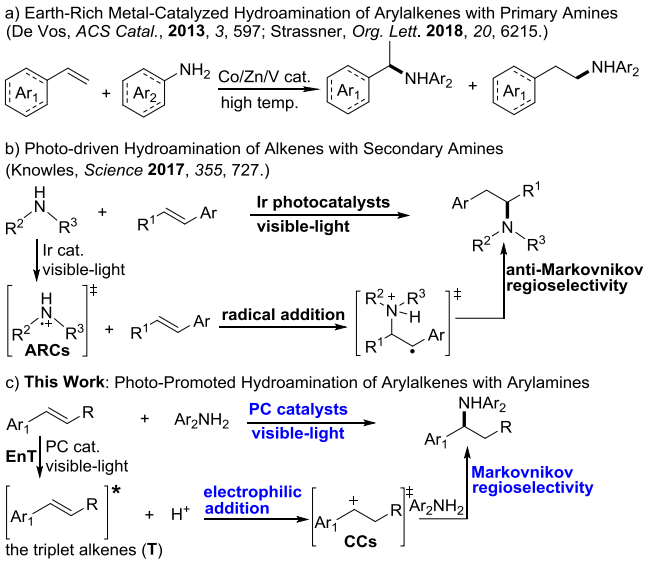
Jiao Gui,[a] Haisheng Xie,[a] Fengjuan Chen,[a] Zhipeng Liu,[a] Xiaoqi Zhang,[b] Fubin Jiang,[c] and Wei Zeng [a,*]

A Bronsted acid/visible-light-promoted Markovnikov hydroamination of vinylarenes with arylamines in the presence of TPT and CF_3CO_2H has been developed. This transformation provides a green approach to *alpha*-amino-substituted arylalkanes under metal-free conditions.

Introduction

α-Arylalkylamines are often encountered in natural products, pharmaceuticals and bioactive small molecules, and also served as useful synthons to construct complex nitrogen-containing organic molecules.[1] In the past decades, great progress has been made to assemble these high value amines through cross-coupling reaction,[2] nucleophilic addition[3] and C-H bond nitrene insertion.[4] In comparison, the direct hydroamination of alkenes with amines provides a 100% atom-efficient method without the formation of byproducts. However, this methodology suffers from high activation barriers and regioselectivity issues.[5] In these regards, earth-rich transition-metal Fe, Co, Ni, Zn, or V-catalyzed hydroamination of olefins could synchronously produce Markovnikov and anti-Markovnikov products under high reaction temperature (**Scheme 1a**).[6] In contrast, regioselectively assembling hydroamination products demands noble metal Rh, Pd or Ir-catalytical system.[7] Thus, there remains a need for exploring a new regioselective hydroamination strategy of alkenes to avoid usage of expensive metal catalysts and harsh conditions.

Recently, visible-light-induced photo catalysis provides a green platform for chemical transformation at ambient temperature, thus also possibly enabling the hydroamination of alkenes by replacing the conventional catalytical approaches. As a consequence, Knowles achieved a significant breakthrough in photo-promoted intermolecular hydroamination of unactive alkenes with secondary alkylamines, in which the excited-state redox Ir-catalysts first oxidized alkylamines to its' aminium radical cations (ARCs), the followed *N*-centered radical addition to alkenes led to the formation of anti-Markovnikov products (**Scheme 1b**).[8] Meanwhile, many works have proved that photocatalytical system could also activate alkenes to form triplet alkenes (**T**) through energy-transfer (EnT).[9] We were therefore aware that the photoexcited alkenes could also trap a proton to produce alkyl carbocations (CCs) in the presence of Bronsted acids, which could subsequently react with amines to afford the corresponding Markovnikov products (**Scheme 1c**).



Scheme 1. Hydroamination strategies of alkenes

Results and discussion

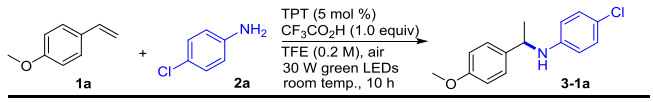
To verify this feasibility, we commenced our investigation by studying the intermolecular hydroamination of 4-methoxystyrene (**1a**) and 4-chloroaniline (**2a**), and found the mixture of **1a** (0.1 mmol), **2a** (0.2 mmol), 2,4,6-triphenylpyrylium tetrafluoroborate (**TPT**, 5 mol %), and

[a]China Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, China
[b]Guangdong Provincial Engineering Research Center for Modernization of TCM, College of Pharmacy, Jinan University, Guangzhou 510632, China
[c]College of Chemistry, Beijing Normal University, Beijing 100875, China
†Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR spectra, mass of the compounds see DOI: 10.1039/x0xx00000x

View Article Online DOI: 10.1039/C9OB02457G

CF_3CO_2H (0.1 mmol) in trifluoroethanol (TFE 1.0 mL) was irradiated with green LEDs (520 nm, 30 W) for 10 h under an air atmosphere at room temperature. α-(*N*-(4-chlorophenyl)amino)-α-(4-meth oxyphenyl)ethane (**3-1a**) was obtained in 81% yield after chromatogaphic isolation (Table 1, entry 1). In comparison, other organo- or noble-metal photo-catalysts such as Eosin Y, $[Mes\text{-}Acr]ClO_4$, Hantzsch ester (HEH), $Ru(bpy)_3Cl_2$ and $[Ir(dtbbpy)(ppy)_2][PF_6]$ gave us considerably lower yields (entries 2-6, 36-57%). Evaluation of different Bronsted acids indicated that the hydroamination reaction of **1a** and **2a** in the presence of TfOH, TsOH and 2,3,4,5-tetrafluoro benzoic acids (TFBA) could occur with lower yields (58-76%) (entries 7-9), and no desired product **3-1a** could be observed in the absence of Bronsted acids (entry 10). Meanwhile, employing 0.2 and 0.5 equ. of CF_3CO_2H led to 16% and 47% yield of **3-1a** (entry 1 vs 11 and 12), respectively, indicating that CF_3CO_2H plays an indispensable role of bronsted acid-catalyst; using blue LEDs as light source led to 50% yield of **3-1a** (entry 13 vs 1). It should be noted that the transformation still afforded 57% and 49% yield of **3-1a** without the photoirradiation and photocatalysts, respectively (entries 14 and 15). These combined facts (entries 1, and 10-15) demonstrated that CF_3CO_2H solely promoted the intermolecular hydroamination of **1a** with **2a** to a certain degree, and the green light possibly induced TPT catalyst to further activate the alkene **1a**, resulting in increased conversions.

Table 1. Optimization of the reaction parameters [a]

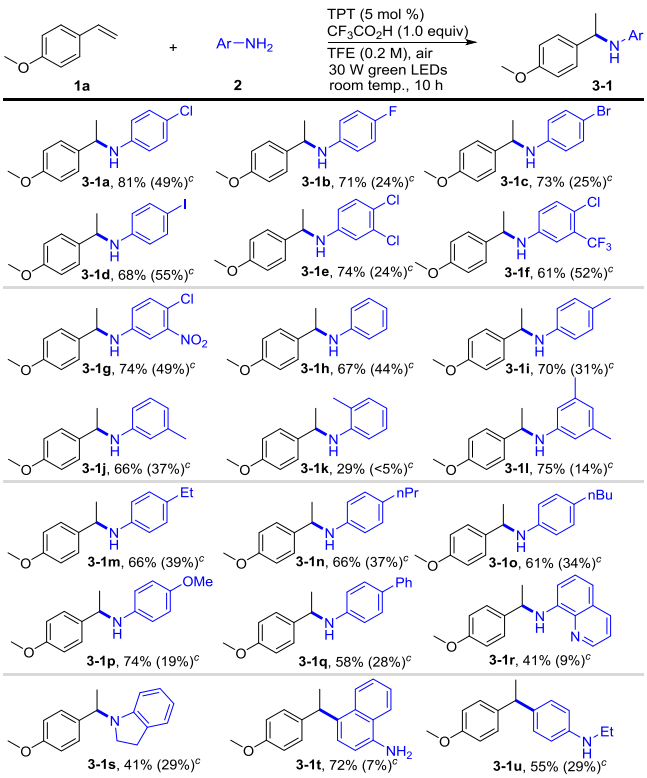


entry	Changes to standard conditions	Yield of 3-1a (%) [b]
1	none	81
2	EosinY	57
3	$[Mes\text{-}Acr]ClO_4$	40
4	HEH	51
5	$Ru(bpy)_3Cl_2$	41
6	$[Ir(dtbbpy)(ppy)_2][PF_6]$	36
7	TfOH	58
8	TsOH	76
9	TFBA	62
10	no acids	0
11	CF_3CO_2H (0.2 equ.)	16
12	CF_3CO_2H (0.5 equ.)	47
13	30 W blue LEDs	50
14	no light	57
15	No PC	49

[a] Reaction conditions: 0.1 mmol of 4-methoxystyrene **1a**, 0.2 mmol of 4-chloroaniline **2a**, photo catalyst TPT (5 mol %), and CF_3CO_2H (1.0 equiv) in TFE (1.0 mL) under an air atmosphere at room temperature for 10 h, green LED light. [b] Isolated yield.

With an optimized protocol in hand, we then examined the substrate scope with respect to the arylamine component (**Scheme 2**). In general, different kinds of halo-substituted arylamines including 4-chlorophenylamine, 4-fluorophenylamine, 4-bromophenylamine, 4-iodophenylamine, and even electron-deficient 4-chloro-3-(trifluoromethyl)aniline and 4-chloro-3-nitroaniline could smoothly react with 4-methoxystyrene **1a** to regioselectively produce the corresponding Markovnikov α-phenylethylamines **3-1a**-**3-1g** in good to excellent yields (61-81%). Meanwhile, electron-rich arylamines such as *para*- or *meta*-alkyl- and *para*- methoxy-substituted anilines could also be efficiently converted into the target hydroamination products **3-1i**, **3-1j**, **3-1l**-**3-1p** in 61-75% yields. However, 2-methylaniline only gave us 29% yield of **3-1k** due to steric hindrance. Gratifyingly, 4-phenylaniline, heteroarylamines (8-aminoquinoline and indoline) could still undergo highly regioselective hydroamination with alkene **1a** to furnish moderate yields of **3-1q**-**3-1s** (41-58%). Notably, when 1-aminonaphthalene and *N*-ethylaniline were subjected to this photocatalytic system, an unexpected reductive coupling between aryl Csp_2-H bonds and alkenes occurred at the *para*-positin of amino group possibly due to the electron-rich property and steric hindrance of arylamines, providing the corresponding arylalkylation products **3-1t** (72%) and **3-1u** (55%), respectively.

Scheme 2. Arylamine scope [a, b]



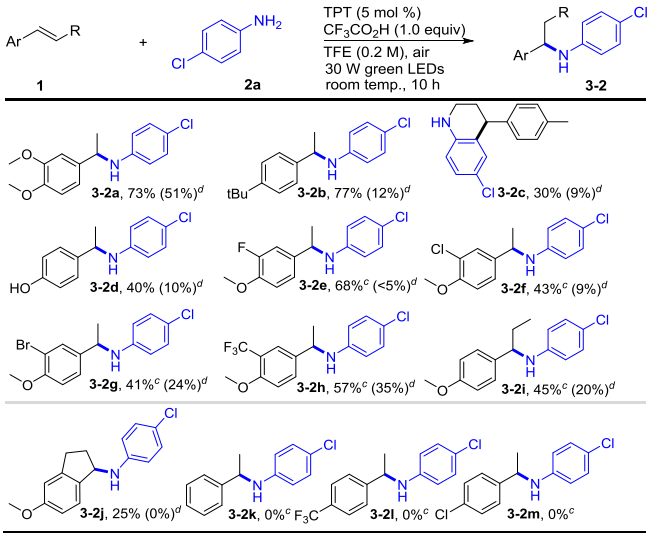
[a] Reaction conditions: 0.1 mmol of 4-methoxystyrene **1a**, 0.2 mmol of arylamines **2**, TPT (5 mol %), and CF_3CO_2H (1.0 equiv) in TFE (1.0 mL) under an air atmosphere at room temperature

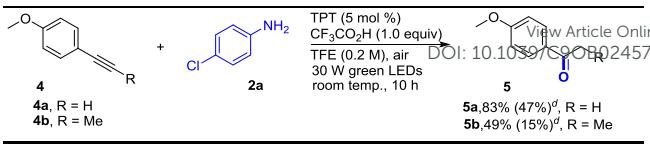
DOI: 10.1039/C9OB02457C

for 10 h, green LED light. [b] Isolated yield. [c] Isolated yield in the absence of TPT.

We next evaluated this transformation of 4-chloroaniline **2a** with various alkenes (**Scheme 3**), and found electron-rich alkenes such as 3,4-dimethoxystyrene and 4-(*tert*-butyl)styrene could furnish the respective hydroamination products **3-2a** (73%) and **3-2b** (77%), respectively. Interestedly, the reaction between 4-methylstyrene and 4-chloroaniline **2a** gave a coupling-cyclization product 1, 2, 3, 4-tetrahydro quinoline **3-2c** (30%) instead of *N*-branched α-arylalkylamine, possibly due to that the solvent CF_3CH_2OH was oxidized into aldehydes, followed by the detrifluoromethylation and condensation with **2a** and cyclozation with 4-methylstyrene.[10] 4-Hydroxylstyrene only gave 40% yield of **3-2d** at room temperature. On the contrary, 3-fluoro-4-methoxystyrene, 3-chloro-4-methoxystyrene, 3-bromo-4-methoxystyrene and 3-trifluoromethyl-4-methoxystyrene underwent moderate conversions only under heating conditions (80 °C), affording 41-68% yields of α-arylalkyl amines **3-2e** ~ **3-2h**.[11] To our delight, when internal alkenes such as 1-(4-methoxyphenyl)-1-propene and 6-methoxy-1H-indene were employed as substrates to react with arylamine **2a**, α-aryl alkylamines **3-2i** (45%) and **3-2j** (25%) could be still obtained through high-regio selective hydroamination. Unfortunately, when electron-neutral and electron-deficient vinylarenes such as styrene, 1-(trifluoromethyl)-4-vinylbenzene, and 1-chloro-4-vinylbenzene were subjected to the standard reaction conditions, no desired α-arylalkylamines **3-2k**, **3-2l**, and **3-2m** were observed, Finally, we tried the hydroamination of electron-rich terminal and internal alkynes **4a** and **4b** with arylamine **2a** under **TPT**-photocatalytic system, and found arylalkylketones **5a** (83%) and **5b** (49%) could be obtained through tandem enamine-ketoimine isomerization and hydrolysis.

Scheme 3. Alkene scope [a, b]





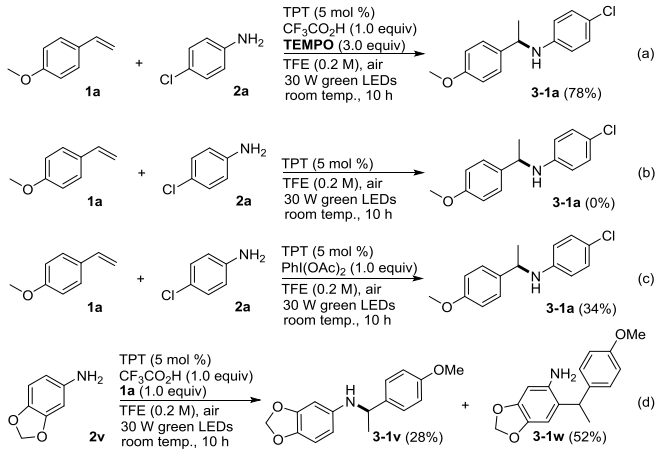
[a] Reaction conditions: 0.1 mmol of aryl unsaturated carbons **1**, 0.2 mmol of 4-chloroaniline **2a**, TPT (5 mol %), and CF_3CO_2H (1.0 equiv) in TFE (1.0 mL) under an air atmosphere at room temperature for 10 h, green LED light. [b] Isolated yield. [c] 80 °C for 24 h. [d] Isolated yield in the absence of TPT.

To ascertain mechanistic insights, we first performed the photocatalyzed hydroamination of 4-methoxystyrene **1a** with 4-chloroaniline **2a** in the presence of **TEMPO** (3.0 equiv), and 78% yield of **3-1a** was obtained, indicating that a single-electron transfer (**SET**) photoredox process was not possibly involved in the transformation (**Scheme 4a**). Subsequently, the photocatalyzed hydroamination of styrene **1a** with arylamine **2a** did not occur in the absence of CF_3CO_2H (**Scheme 4b**), but employing $PhI(OAc)_2$ could still furnish 34% yield of **3-1a** (**Scheme 4c**), these two control experiments implied that Bronsted acids or Lewis acids could interact with arylamines to form activated aminium ion intermediates.[12] Moreover, employing strong electron-donating methylenedioxy group substituted aniline (**2v**) as a substrate to react with 4-methoxystyrene **1a** synchronously gave hydroamination product **3-1v** (28%) and arylalkylation product **3-1w** (52%) (**Scheme 4d**), indicating benzyl carboncations were also possibly involved in this transformation.

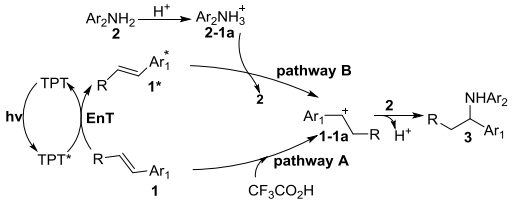
On the other hand, Stern-Volmer fluorescence quenching analysis suggested that photoexcited **TPT*** was quenched mainly by styrene **1a**. On the contrary, the representative amine **2a** and CF_3CO_2H did not decrease the phosphorescene intensity of photoexcited **TPT*** (**Fig. S-1, S-2, S-3, and S-4** in SI). Meanwhile, the UV-visible spectrum of 4-methoxystyrene (**1a**) displayed a maximum absorption at around 220-320 nm (**Fig. S-5** in SI). Although the emission spectrum (420-600 nm) of TPT photocatalyst which was irradiated by 410 nm light (see **Fig. S-6**), was not overlapped with the UV-absorption spectrum of **1a**, when the TPT catalyst was irradiated by 490, 500, and 520 nm, respectively, a new emission spectrum at around 290-330 nm from TPT was observed (**Fig. S-7**). The partial overlap between the UV-absorption spectrum (around 220-320 nm) of **1a** and the emission spectrum (290-330 nm) of TPT indicated that the energy transfer process from excited TPT* to vinylarenes possibly occurred in this Markovnikov hydroamination.

Scheme 4. Preliminary mechanistic studies

DOI: 10.1039/C9OB02457G



The above-mentioned experiments, Stern-Volmer and spectral analysis indicated that two reaction pathways were involved in this transformation (**Scheme 5)**. At first, the traditional Bronsted acid-promoted Markovnikov hydroamination belongs to reaction pathway **A**. Another reaction pathway **B** was involved in the visible-light-assisted hydroamination, which started with the photoexcitation of TPT to produce the excited state **TPT***, then **TPT*** activated styrene **1** and generate excited triplet styrene **1*** via EnT process. Meanwhile, the interaction of Bronsted acid (CF_3CO_2H) with Ar_2NH_2 **2** resulted in the formation of aminium ion $Ar_2NH_3^+$ (**2-1a**), whose proton could be captured by photoexcited styrene **1*** to produce benzylic carbocation species **1-1a** through electrophilic addition.[13] Finally, the coupling reaction of carbocation species **1-1a** with arylamine **2** gave the Markovnikov hydroamination product **3** with the release of protons.



Scheme 5. The possible reaction mechanism

Conclusions

In conclusion, we have developed a CF_3CO_2H/visible-light-promoted reductive coupling-reaction between aryl alkenes and arylamines for assembly of α-arylalkyl amines. The present approach is operationally simple and does not require any metal catalysts, thus featuring a highly regioselective Markovnikov addition. Furthermore, the control experiments demonstrated that CF_3CO_2H and visible-light-catalysis play a complementary role in producing carboncation intermediates.

Experimental Section

General Information

General Methods. All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using silica gel (300-400 mesh). Infrared spectra (IR) are reported as wavelength numbers (cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance DPX 600 fourier Transform spectrometer operating at 400 MHz or 500 MHz for ^1H NMR and 100 MHz or 125 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using a Waters HPLC/ZQ4000 Mass Spectrometer. High resolution mass spectra (HR-MS) were recorded on an IF-TOF spectrometer (Micromass). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer..

General Procedure for the Visivle-Light-Promoted Markovnikov Hydroamination of Arylalkenes with Arylamines

A flame-dried Schlenk tube (25 mL) equipped with a magnetic stirrer bar was charged sequentially with 0.1 mmol of styrenes **1**, 0.2 mmol of arylamines **2**, photo catalysts TPT (5 mol %), and CF_3CO_2H (1.0 equiv) in TFE (1.0 mL) under air atmosphere. Then the mixture was stirred and irradiated with 2 × 30 W blue LEDs at room temperature for 10 h. The mixture was then filtered through a short Celite pad. The filtrate was concentrated, and the product was purified by column chromatography on silica gel (hexanes/ethyl acetate) to afford the desired products **3**.

4-Chloro-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1a)[14]: Yellow oil, 21.2 mg, 81% yield (without TPT, 14.9 mg, 49% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.34 (d, *J* = 8.6 Hz, 2H), 4.31 (q, *J* = 6.6 Hz, 1H), 3.70 (s, 3H), 1.40 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 145.9, 136.7, 128.9, 126.9, 121.8, 114.5, 114.1, 55.3, 53.0, 24.9; MS(ESI): m/z = 261.1 [M^+], IR (KBr): 3415, 2963, 2927, 2835, 1599, 1510, 1499, 1247, 1177, 815, 749 cm^{-1}.

4-Fluoro-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1b): Yellow oil, 17.4 mg, 71% yield (without TPT, 6 mg, 24% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.1 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.71 (t, *J* = 8.7 Hz, 2H), 6.35 (dd, *J* = 8.8, 4.4 Hz, 2H), 4.29 (q, *J* = 6.6 Hz, 1H), 3.70 (s, 3H), 1.40 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 156.8 (d, *J* = 233.3 Hz), 143.7, 137.1(d, *J* = 1.4 Hz), 126.9, 115.6 (d, *J* = 22.1 Hz), 114.2(d, *J* = 7.3 Hz), 114.1, 55.3, 53.5, 25.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.32; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{15}H_{17}FNO$: 246.1289, found: 246.1289; IR (KBr): 3423, 2963, 2836, 1612, 1510, 1276, 1245, 1219, 820, 764, 750 cm^{-1}.

4-Bromo-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1c)[15]: Yellow oil, 22.3 mg, 73% yield (without TPT, 7.6 mg, 25% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.29 (d, *J* = 8.7 Hz, 2H), 4.30 (q, *J* = 6.7 Hz, 1H), 3.87 (s, 1H, NH), 3.69 (s, 3H), 1.39 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 146.3, 136.7, 131.8, 126.9,

115.0, 114.1, 108.8, 55.3, 52.9, 25.0; MS(ESI): m/z = 305.0 [M^+]; IR (KBr): 3415, 2962, 2927, 2834, 1593, 1510, 1496, 1246, 1177, 811, 764, 750 cm^{-1}.

4-Iodo-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1d): Yellow oil, 24.0 mg, 68% yield (without TPT, 19.4 mg, 55% yield); ^1H NMR (400 MHz, CDCl3) δ 7.32 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 2H), 6.28 (d, *J* = 7.6 Hz, 2H), 4.39 (q, *J* = 6.6 Hz, 1H), 3.78 (s, 3H), 1.48 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 158.6, 146.8, 137.6, 136.6, 126.8, 115.6, 114.1, 77.8, 55.3, 52.8, 24.9; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{15}H_{17}INO$: 354.0349, found: 354.0343; IR (KBr): 2929, 2833, 1594, 1510, 1275, 1261, 1177, 832, 764, 750 cm^{-1}.

3,4-Dichloro-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1e): Yellow oil, 21.9 mg, 74% yield (without TPT, 7 mg, 24% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.57 (s, 1H), 6.32 (d, *J* = 8.7 Hz, 1H), 4.37 (q, *J* = 6.5 Hz, 1H), 4.07 (s, 1H, NH), 3.78 (s, 3H), 1.47 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 146.8, 136.1, 132.6, 130.5, 126.8, 119.7, 114.5, 114.2, 112.9, 55.3, 52.9, 24.8; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{15}H_{16}Cl_2NO$: 296.0603, found: 296.0606; IR (KBr): 3419, 2963, 2928, 2835, 1597, 1511, 1492, 1320, 1244, 1175, 1132, 1036, 830, 808, 666 cm^{-1}.

4-Chloro-*N*-(1-(4-methoxyphenyl)ethyl)-3-(trifluoromethyl)aniline (3-1f): Yellow oil, 20.1 mg, 61% yield (without TPT, 17 mg, 52% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 1H), 6.93 – 6.85 (m, 3H), 6.54 (d, *J* = 8.6 Hz, 1H), 4.45 (q, *J* = 6.2 Hz, 1H), 4.26 (s, 1H, NH), 3.82 (s, 3H), 1.53 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 145.8, 135.9, 131.9, 126.8, 121.6, 118.7 (d, *J* = 2.2 Hz), 116.5, 114.3, 112.2 (q, *J* = 5.6 Hz), 55.3, 53.0, 24.8; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{16}H_{16}ClF_3NO$: 330.0867, found: 330.0864; IR (KBr): 3412, 2964, 2930, 2838, 1612, 1511, 1487, 1341, 1247, 1174, 1133, 1025, 830, 814, 671 cm^{-1}.

4-Chloro-*N*-(1-(4-methoxyphenyl)ethyl)-3-nitroaniline (3-1g): Yellow oil, 22.7 mg, 74% yield (without TPT, 15 mg, 49% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.95 (s, 1H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 1H), 4.41 (q, *J* = 5.3 Hz, 1H), 4.35 (s, 1H, NH), 3.78 (s, 3H), 1.51 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 148.4, 146.5, 135.3, 131.9, 126.8, 117.7, 114.4, 113.5, 109.2, 55.3, 53.0, 24.6; HR-MS (ESI) calcd for [M + Na]+: $C_{15}H_{16}ClN_2NaO_3$: 329.0663, found: 329.0665; IR (KBr): 3412, 2964, 2929, 2836, 1611, 1533, 1511, 1332, 1246, 1176, 1035, 831, 817, 752, 685 cm-1.

***N*-(1-(4-Methoxyphenyl)ethyl)aniline (3-1h)**[16]: Yellow oil, 15.2 mg, 67% yield (without TPT, 9.9 mg, 44% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 2H), 6.77 (d, *J* = 7.9 Hz, 2H), 6.67 (t, *J* = 6.9 Hz, 1H), 6.57 (d, *J* = 7.4 Hz, 2H), 4.38 (q, *J* = 6.6 Hz, 1H), 3.70 (s, 3H), 1.49 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 147.4, 137.3, 129.1, 127.0, 117.3, 114.1, 113.4, 55.3, 52.9, 25.0; MS(ESI): m/z= 227.1 [M^+]; IR (KBr): 3407, 2960, 2923, 2835, 1603, 1508, 1244, 1178, 1034, 830, 750, 693 cm^{-1}.

***N*-(1-(4-Methoxyphenyl)ethyl)-4-methylaniline (3-1i)**[17]: Yellow oil, 16.9 mg, 70% yield (without TPT, 7.5 mg, 31% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.50 (d, *J* = 8.3 Hz, 2H), 4.47 (q, *J* = 6.6 Hz, 1H), 3.83 (s, 3H), 2.24 (s, 3H), 1.53 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 145.1, 137.5, 129.6, 127.0, 126.4, 114.0, 113.6, 55.3, 53.1, 25.0, 20.4; MS(ESI): m/z = 241.2 [M^+]; IR (KBr): 3408, 2961, 2923, 2865, 2834, 1614, 1518, 1300, 1245, 1178, 1036, 830, 808, 750 cm^{-1}.

***N*-(1-(4-Methoxyphenyl)ethyl)-3-methylaniline (3-1j)**: Yellow oil, 15.9 mg, 66% yield (without TPT, 8.9 mg, 37% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.53 (d, *J* = 7.4 Hz, 1H), 6.42 (s, 1H), 6.37 (d, *J* = 8.1 Hz, 1H), 4.50 (q, *J* = 6.6 Hz, 1H), 3.83 (s, 3H), 2.27 (s, 3H), 1.53 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 147.4, 138.8, 137.4, 129.0, 127.0, 118.2, 114.3, 114.0, 110.4, 55.3, 52.8, 24.9, 21.6; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{16}H_{20}NO$: 242.1539, found: 242.1535; IR (KBr): 3403, 2961, 2924, 2834, 1607, 1587, 1510, 1488, 1244, 1176, 1036, 830, 769, 692 cm^{-1}.

***N*-(1-(4-Methoxyphenyl)ethyl)-2-methylaniline (3-1k)**: Yellow oil, 7.0 mg, 29% yield (without TPT, trace yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.87 (t, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 2H), 6.50 (t, *J* = 7.3 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 1H), 4.40 (q, *J* = 6.3 Hz, 1H), 3.71 (s, 1H, NH), 3.67 (s, 3H), 2.11 (s, 3H), 1.44 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 145.3, 137.4, 130.0, 127.0, 126.9, 121.6, 116.8, 114.1, 111.1, 55.3, 52.7, 25.3, 17.7; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{16}H_{20}NO$: 242.1539, found: 242.1537; IR (KBr): 3429, 2961, 2927, 2834, 1606, 1585, 1511, 1444, 1314, 1246, 1174, 1036, 829, 748 cm^{-1}.

***N*-(1-(4-Methoxyphenyl)ethyl)-3,5-dimethylaniline (3-1l)**: Yellow oil, 19.2 mg, 75% yield (without TPT, 3.6 mg, 14% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 8.1 Hz, 2H), 6.23 (s, 1H), 6.09 (s, 2H), 4.36 (q, *J* = 6.4 Hz, 1H), 3.70 (s, 3H), 2.09 (s, 6H), 1.39 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 147.5, 138.7, 137.5, 127.0, 119.3, 114.0, 111.3, 55.3, 52.7, 24.9, 21.5; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{17}H_{22}NO$: 256.1696, found: 256.1692; IR (KBr): 3401, 2960, 2922, 2856, 1603, 1510, 1338, 1244, 1180, 1035, 827, 749 cm^{-1}.

4-Ethyl-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1m): Yellow oil, 16.8 mg, 66% yield (without TPT, 10 mg, 39% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.1 Hz, 2H), 4.48 (q, *J* = 6.6 Hz, 1H), 3.84 (s, 3H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.54 (d, *J* = 6.7 Hz, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 145.4, 137.6, 133.0, 128.5, 127.0, 114.0, 113.5, 55.3, 53.2, 27.9, 25.1, 15.9; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{17}H_{22}NO$: 256.1696, found: 256.1694; IR (KBr): 3407, 2961, 2928, 2869, 1614, 1517, 1300, 1245, 1179, 1036, 827 cm^{-1}.

***N*-(1-(4-Methoxyphenyl)ethyl)-4-propylaniline (3-1n)**: Yellow oil, 17.8 mg, 66% yield (without TPT, 10.0 mg, 37% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 7.7 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 7.8 Hz, 2H), 4.40 (q, *J* = 6.5 Hz, 1H), 3.76 (s, 3H), 2.42 (t, *J* = 7.6 Hz, 2H), 1.55 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.46 (d, *J* = 6.6 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 145.4, 137.6, 131.5, 129.1, 127.0, 114.0, 113.4, 55.3, 53.1, 37.2, 25.1, 24.9, 13.9; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{18}H_{24}NO$: 270.1852, found: 270.1844; IR (KBr): 3409,

2958, 2927, 2869, 1614, 1515, 1301, 1244, 1179, 1037, 829, 750 cm^{-1}.

4-Butyl-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1o): Yellow oil, 17.3 mg, 61% yield (without TPT, 9.6 mg, 34% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.44 (d, *J* = 7.4 Hz, 2H), 4.40 (q, *J* = 6.4 Hz, 1H), 3.77 (s, 3H), 2.44 (t, *J* = 7.5 Hz, 2H), 1.55 – 1.44 (m, 5H), 1.35 – 1.24 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 145.3, 137.6, 131.6, 129.0, 127.0, 114.0, 113.4, 55.3, 53.1, 34.7, 34.0, 25.1, 22.4, 14.0; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{19}H_{26}NO$: 284.2009, found: 284.2004; IR (KBr): 3409, 2958, 2927, 2869, 1614, 1515, 1301, 1244, 1179, 1037, 829, 750 cm^{-1}.

4-Methoxy-*N*-(1-(4-methoxyphenyl)ethyl)aniline (3-1p)[18]: Yellow oil, 19.0 mg, 74% yield (without TPT, 4.9 mg, 19% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.53 (d, *J* = 8.5 Hz, 2H), 4.43 (q, *J* = 6.6 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 1.52 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 152.0, 141.6, 137.5, 127.0, 114.8, 114.7, 114.0, 55.8, 55.3, 53.7, 25.1; MS(ESI): m/z=257.1 [M$^+$]; IR (KBr): 3397, 2959, 2931, 2833, 1611, 1511, 1241, 1177, 1037, 820, 758 cm^{-1}.

***N*-(1-(4-Methoxyphenyl)ethyl)-[1,1'-biphenyl]-4-amine (3-1q)**: Yellow oil, 17.6 mg, 58% yield (without TPT, 8.5 mg, 28% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.0 Hz, 4H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.24 – 7.17 (m, 1H), 6.85 (d, *J* = 7.7 Hz, 2H), 6.56 (d, *J* = 7.6 Hz, 2H), 4.47 (q, *J* = 6.5 Hz, 1H), 4.06 (s, 1H, NH), 3.76 (s, 3H), 1.49 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 146.9, 141.3, 137.2, 130.1, 128.7, 127.9, 127.0, 126.3, 126.0, 114.1, 113.6, 55.3, 52.9, 25.1; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{21}H_{22}NO$: 304.1696, found: 304.1683; IR (KBr): 3409, 3025, 2962, 2928, 2834, 1612, 1524, 1511, 1489, 1322, 1299, 1245, 1177, 1036, 827, 763, 698 cm^{-1}.

***N*-(1-(4-Methoxyphenyl)ethyl)quinolin-8-amine (3-1r):** Yellow oil, 11.4 mg, 41% yield (without TPT, 2.5 mg, 9% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 2.1 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.39 (t, *J* = 9.0 Hz, 3H), 7.26 (t, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.58 (s, 1H, NH), 6.46 (d, *J* = 7.6 Hz, 1H), 4.66 (m, 1H), 3.80 (s, 3H), 1.70 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 146.8, 143.7, 138.2, 137.2, 136.1, 128.6, 127.7, 126.9, 121.3, 114.0, 113.9, 106.2, 55.3, 52.7, 25.2; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{18}H_{19}N_2O$: 279.1492, found: 279.1490; IR (KBr): 3394, 2960, 2922, 2849, 1611, 1575, 1518, 1479, 1379, 1245, 1172, 1035, 830, 818, 791, 747 cm^{-1}.

1-(1-(4-Methoxyphenyl)ethyl)indoline (3-1s): Yellow oil, 10.4 mg, 41% yield (without TPT, 7.3 mg, 29% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.1 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 4.74 (q, *J* = 6.6 Hz, 1H), 3.84 (s, 3H), 3.40 (q, *J* = 9.0 Hz, 1H), 3.31 (q, *J* = 7.8 Hz, 1H), 2.97 (t, *J* = 8.4 Hz, 2H), 1.55 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 151.5, 134.9, 130.2, 128.2, 127.2, 124.4, 116.9, 113.7, 107.2, 55.3, 53.8, 47.8, 28.2, 16.4; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{17}H_{20}NO$: 254.1539, found: 254.1540; IR (KBr): 2963, 2930, 2834, 1607, 1512, 1487, 1302, 1248, 1178, 1031, 832, 743 cm^{-1}.

4-(1-(4-Methoxyphenyl)ethyl)naphthalen-1-amine (3-1t): Yellow oil, 20.0 mg, 72% yield (without TPT, 1.9 mg, 7% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.77 (m, 2H), 7.52 – 7.40 (m, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 7.9 Hz, 2H), 4.30 (q, *J* = 7.0 Hz, 1H), 4.11 (s, 2H, NH), 3.81 (s, 3H), 1.75 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 138.8, 137.7, 133.1, 128.5, 125.8, 125.2, 124.9, 124.1, 123.8, 120.5, 118.4, 114.1, 55.3, 39.5, 21.9; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{19}H_{20}NO$: 278.1539, found: 278.1540; IR (KBr): 3460, 3387, 3057, 2963, 2930, 2834, 1621, 1509, 1400, 1245, 1178, 1031, 832, 803, 748 cm^{-1}.

***N*-Ethyl-4-(1-(4-methoxyphenyl)ethyl)aniline (3-1u)**: Yellow oil, 14.0 mg, 55% yield (without TPT, 7.5 mg, 29% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 8.4 Hz, 2H), 3.92 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 1H, NH), 3.69 (s, 3H), 3.05 (q, *J* = 7.1 Hz, 2H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 146.5, 139.5, 135.8, 128.4, 128.3, 113.7, 112.9, 55.3, 43.1, 38.8, 22.3, 14.9; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{17}H_{22}NO$: 256.1696, found: 256.1689; IR (KBr): 2963, 2920, 1611, 1510, 1245, 1177, 1033, 831, 749 cm^{-1}.

***N*-(1-(4-Methoxyphenyl)ethyl)benzo[d][1,3]dioxol-5-amine (3-1v)**: Yellow oil, 7.6 mg, 28% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 8.3 Hz, 1H), 6.14 (s, 1H), 5.94 (d, *J* = 8.3 Hz, 1H), 5.78 (s, 2H), 4.34 (q, *J* = 6.4 Hz, 1H), 3.77 (s, 3H), 1.45 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 148.1, 143.1, 139.4, 137.3, 126.9, 114.0, 108.5, 105.2, 100.5, 96.4, 55.3, 53.7, 25.1; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{16}H_{18}NO_3$: 272.1281, found: 272.1287; IR (KBr): 3410, 2961, 2921, 2850, 1633, 1611, 1504, 1488, 1285, 1244, 1210, 1178, 1038, 934, 831, 813, 789 cm^{-1}.

6-(1-(4-Methoxyphenyl)ethyl)benzo[d][1,3]dioxol-5-amine (3-1w): Yellow oil, 14.1 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.9 Hz, 2H), 6.85 – 6.77 (m, 3H), 6.24 (s, 1H), 5.85 (s, 2H), 3.96 (q, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 3.24 (s, 2H, NH), 1.53 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 146.2 140.6, 138.6, 137.8, 128.3, 122.8, 114.1, 107.4, 100.6, 98.6, 55.3, 39.1, 22.2; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{16}H_{18}NO_3$: 272.1281, found: 272.1281; IR (KBr): 3442, 3367, 2962, 2929, 2835, 1633, 1609, 1507, 1485, 1244, 1172, 1037, 932, 831, 750 cm^{-1}.

4-Chloro-*N*-(1-(3,4-dimethoxyphenyl)ethyl)aniline (3-2a): Yellow oil, 21.3 mg, 73% yield (without TPT, 14.9 mg, 51% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.5 Hz, 2H), 6.87 (d, *J* = 10.3 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.42 (d, *J* = 7.5 Hz, 2H), 4.36 (q, *J* = 6.5 Hz, 1H), 4.02 (s, 1H, NH), 3.84 (s, 6H), 1.48 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 148.0, 145.9, 137.4, 128.9, 121.8, 117.7, 114.5, 111.4, 109.0, 55.9, 53.4, 25.0; HR-MS (ESI) calcd for [M + 1]$^+$: $C_{16}H_{19}ClNO_2$: 292.1099, found: 292.1091; IR (KBr): 3404, 2961, 2932, 2834, 1599, 1515, 1499, 1316, 1256, 1169, 1027, 814, 764 cm^{-1}.

***N*-(1-(4-(*tert*-Butyl)phenyl)ethyl)-4-chloroaniline (3-2b)**: Yellow oil, 22.2 mg, 77% yield (without TPT, 3.5 mg, 12% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 6.49 (d, *J* = 7.7 Hz, 2H), 4.48 (q, *J* = 6.5 Hz, 1H), 4.08 (s, 1H, NH), 1.55 (d, *J* = 6.5 Hz, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 146.0, 141.6, 129.0, 125.6,

125.5, 121.7, 114.4, 53.2, 34.5, 31.5, 24.8; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{18}H_{23}ClN$: 288.1441, found: 288.1429; IR (KBr): 3418, 3023, 2962, 2903, 2867, 1600, 1497, 1316, 1295, 1252, 1177, 1091, 1015, 832, 814, 677, 576 cm^{-1}.

6-Chloro-4-(*p*-tolyl)-1,2,3,4-tetrahydroquinoline (3-2c): Yellow oil, 7.7 mg, 30% yield (without TPT, 2.5 mg, 9% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.75 (s, 1H), 6.48 (d, *J* = 8.5 Hz, 1H), 4.08 (t, *J* = 6.0 Hz, 1H), 3.34 – 3.21 (m, 2H), 2.36 (s, 3H), 2.23 – 2.14 (m, 1H), 2.08 – 1.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.8, 136.0, 129.9, 129.2, 128.5, 127.2, 125.2, 121.5, 115.3, 42.3, 39.1, 30.7, 21.0; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{16}H_{17}ClN$: 258.1044, found: 258.1036; IR (KBr): 3415, 2922, 2851, 1601, 1496, 1353, 1297, 1263, 1084, 809, 765 cm^{-1}.

4-(1-((4-Chlorophenyl)amino)ethyl)phenol (3-2d): Yellow oil, 9.9 mg, 40% yield (without TPT, 2.5 mg, 10% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 7.9 Hz, 2H), 6.41 (d, *J* = 8.0 Hz, 2H), 4.54 (s, 1H, NH), 4.37 (q, *J* = 6.6 Hz, 1H), 1.46 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 145.8, 136.9, 128.9, 127.1, 121.8, 115.6, 114.5, 53.0, 25.0; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{14}H_{15}ClNO$: 248.0837, found: 248.0836; IR (KBr): 3589, 3450, 3022, 2965, 2925, 2868, 1612, 1598, 1512, 1497, 1316, 1252, 1176, 1092, 1012, 832, 816, 739 cm^{-1}.

4-Chloro-*N*-(1-(3-fluoro-4-methoxyphenyl)ethyl)aniline (3-2e): Yellow oil, 19.0 mg, 68% yield (without TPT, trace yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.00 (m, 4H), 6.90 (t, *J* = 8.5 Hz, 1H), 6.40 (d, *J* = 8.5 Hz, 2H), 4.36 (q, *J* = 6.5 Hz, 1H), 4.00 (s, 1H, NH), 3.86 (s, 3H), 1.47 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4 (d, *J* = 10.7 Hz), 145.6, 138.0 (d, *J* = 4.9 Hz), 129.0, 122.1, 121.3 (d, *J* = 3.1 Hz), 114.4, 113.7 (d, *J* = 1.0 Hz), 113.6, 113.5, 56.4, 52.8, 25.0; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{15}H_{16}ClFNO$: 280.0899, found: 280.0896; IR (KBr): 3412, 2964, 2928, 2850, 1600, 1518, 1499, 1295, 1274, 1133, 1028, 815, 761 cm^{-1}.

4-Chloro-*N*-(1-(3-chloro-4-methoxyphenyl)ethyl)aniline (3-2f): Yellow oil, 12.7 mg, 43% yield (without TPT, 2.8 mg, 9% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.40 (d, *J* = 8.5 Hz, 2H), 4.35 (q, *J* = 6.6 Hz, 1H), 3.99 (s, 1H, NH), 3.86 (s, 3H), 1.45 (d, *J* = 9.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 145.6, 138.0, 129.0, 127.7, 125.0, 122.7, 122.0, 114.5, 112.3, 56.2, 52.8, 25.0; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{15}H_{16}Cl_2NO$: 296.0603, found: 296.0606; IR (KBr): 3417, 2965, 2927, 2838, 1600, 1503, 1316, 1290, 1256, 1202, 1178, 1091, 1063, 1021, 814, 739 cm^{-1}.

***N*-(1-(3-Bromo-4-methoxyphenyl)ethyl)-4-chloroaniline (3-2g)**: Yellow oil, 14.0 mg, 41% yield (without TPT, 8 mg, 24% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 1.9 Hz, 1H), 7.22 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.40 (d, *J* = 8.8 Hz, 2H), 4.35 (q, *J* = 6.6 Hz, 1H), 3.99 (s, 1H, NH), 3.86 (s, 3H), 1.47 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 154.9, 145.6, 138.5, 130.8, 129.0, 125.7, 122.1, 114.5, 112.2, 112.0, 56.3, 52.7, 25.0; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{15}H_{16}BrClNO$: 340.0098, found: 340.0081; IR (KBr): 3415, 2963, 2927, 2838, 1600, 1497, 1315, 1286, 1255, 1053, 1020, 814, 736, 680, 552 cm-1.

4-Chloro-*N*-(1-(4-methoxy-3-(trifluoromethyl)phenyl)ethyl)aniline (3-2h): Yellow oil, 18.8 mg, 57% yield (without TPT, 11.5 mg, 35% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.32 (d, *J* = 8.8 Hz, 2H), 4.33 (q, *J* = 6.6 Hz, 1H), 3.94 (s, 1H, NH), 3.80 (s, 3H), 1.41 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5 (q, *J* = 1.7 Hz), 145.5, 136.5, 130.4, 129.0, 124.6 (q, *J* = 5.2 Hz), 122.2, 119.1, 114.5, 112.4, 56.0, 52.9, 25.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.30; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{16}H_{16}ClF_3NO$: 330.0867, found: 330.0867; IR (KBr): 3422, 2967, 2931, 2843, 1620, 1599, 1504, 1324, 1277, 1258, 1129, 1057, 1024, 817, 677 cm^{-1}.

4-Chloro-*N*-(1-(4-methoxyphenyl)propyl)aniline (3-2i): Yellow oil, 12.4 mg, 45% yield (without TPT, 5.5 mg, 20% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.42 (d, *J* = 8.3 Hz, 2H), 4.12 (t, *J* = 6.4 Hz, 1H), 4.04 (s, 1H, NH), 3.78 (s, 3H), 1.88 – 1.70 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 146.1, 135.3, 128.9, 127.5, 121.6, 114.4, 114.0, 59.3, 55.3, 31.6, 10.8; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{16}H_{19}ClNO$: 276.1150, found: 276.1155; IR (KBr): 3430, 2960, 2920, 2850, 1608, 1509, 1497, 1302, 1245, 1175, 1090, 1032, 814, 749 cm^{-1}.

***N*-(4-Chlorophenyl)-5-methoxy-2,3-dihydro-1H-inden-1-amine (3-2j):** Yellow oil, 6.8 mg, 25% yield (without TPT, 0% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.3 Hz, 1H), 7.16 – 7.14 (m, 1H), 7.13 – 7.11 (m, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 6.76 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.63 – 6.61 (m, 1H), 6.61 – 6.59 (m, 1H), 4.90 (t, *J* = 6.3 Hz, 1H), 3.86 (s, 1H, NH), 3.80 (s, 3H), 3.04 – 2.95 (m, 1H), 2.91 – 2.81 (m, 1H), 2.60 – 2.50 (m, 1H), 1.96 – 1.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 145.4, 136.2, 129.2, 124.9, 114.3, 112.9, 110.0, 58.1, 55.5, 33.9, 30.4; HR-MS (ESI) calcd for $[M + 1]^+$: $C_{16}H_{17}ClNO$: 274.0985, found: 274.1000; IR (KBr): 3444, 2955, 2921, 2849, 1645, 1494, 1467, 1399, 1303, 1256, 1176, 1089, 1032, 814, 747 cm^{-1}.

4-Chloro-*N*-(1-phenylethyl)aniline (3-2k), 4-Chloro-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)aniline (3-2l) and 4-Chloro-*N*-(1-(4-chlorophenyl)ethyl)aniline (3-2m) could not be obtained under our reaction conditions.

1-(4-Methoxyphenyl)ethan-1-one (5a)[19]: Yellow oil, 12.5 mg, 83% yield (without TPT, 7 mg, 47% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 3.87 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 163.5, 130.6, 130.4, 113.7, 55.5, 26.3; MS(ESI): m/z = 150.1 $[M^+]$; IR (KBr): 3339, 3003, 2960, 2932, 2840, 1676, 1599, 1576, 1510, 1358, 1258, 1172, 1028, 957, 834, 806, 592, 577, 564 cm^{-1}.

1-(4-Methoxyphenyl)propan-1-one (5b)[19]: Yellow oil, 8.0 mg, 49% yield (without TPT, 4 mg, 15% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H), 3.86 (s, 3H), 2.95 (q, *J* = 7.0 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 163.3, 130.2, 130.0, 113.7, 55.4, 31.4, 8.5; MS(ESI): m/z = 164.1 $[M^+]$; IR (KBr): 3339, 3004, 2963, 2934, 2850, 1676, 1600, 1576, 1510, 1417, 1359, 1258, 1170, 1028, 959, 832, 807, 590, 578, 560 cm^{-1}.

Acknowledgements

This project has received funding from the NKRDPC (No. 2016YFA0602900, 2017YFC1703802), NFSC (No. 201871097, U1801287), GPSF (No. 2017B090903003) and GNFS (No. 2018B030308007).

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View Article Online
DOI: 10.1039/C9OB02457C

Organic & Biomolecular Chemistry

PAPER

Bronsted Acid/Visible-Light-Promoted Markovnikov Hydroamination of Vinylarenes with Arylamines

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Jiao Gui,Haisheng Xie, Fengjuan Chen, Zhipeng Liu, Xiaoqi Zhang, Fubin Jiang, and Wei Zeng *

Table of Content

A Bronsted acid/visible-light-promoted Markovnikov hydroamination of arylalkenes with arylamines in the presence of TPT and CF_3CO_2H has been developed.