Regioselective Photoamination of 2-Styrylthiophenes with Ammonia

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Photoinduced electron transfer from the singlet excited state of 2-styrylthiophenes (**1a**-**1f**) to *p*-DCB (*p*-dicyanobenzene) has been proposed from the negative value of ΔG_{ET} (the free energy of the electron transfer) calculated by the Rehm-Weller equation. This leads to the formation of radical cations of **1a**-**1f** and a radical anion of *p*-DCB. The *p*-nitro derivative **1g** can not result in the radical cation due to the positive ΔG_{ET} value which results from the unfavorable singlet excitation energy ($E_{0,0}$) and oxidation potential. Regioselective amination by ammonia to the radical cations of **1a**-**1e** has occurred to afford 1-amino-1-aryl-2-(thien-2-yl)ethanes (**2a**-**2e**) in reasonable yields (50-90%). The regioselectivity arises from the attack of ammonia at the localized positive charge on C-1 of the ethene bond of the radical cations of **1a**-**1e**.

Keywords: Photosensitization; Electron transfer; Nucleophilic addition; Regioselectivity.

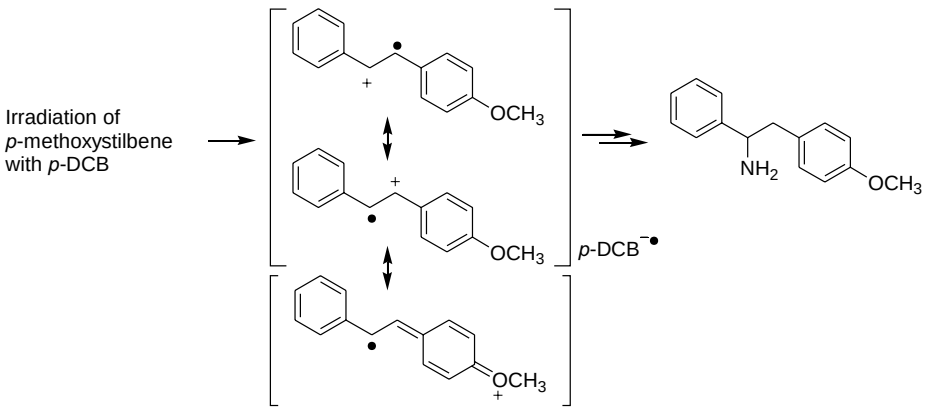
INTRODUCTION

Photoaddition of nucleophiles to the electron rich substrates,[1,2] such as styrenes,[3] stilbenes,[4] and arenes,[5] via photoinduced electron transfer is a potentially useful synthetic procedure. And photoamination reactions can provide convenient ways for the synthesis of primary and secondary amines[5] directly. It is also a useful tool for the synthesis of isoquinolines[6] and aporphines.[7]

Regioselectivity for the substituent depended photoamination of stilbenes with ammonia in the presence of *p*-dicyanobenzene (*p*-DCB) has been investigated.[4] The oxygen atom of the *para* methoxy group in stilbenes has played an important role in localizing the appropriate positive charge in one of the intermediates. Thus addition of ammonia is limited to the other position of the radical cation intermediate. Therefore photoamination of *p*-methoxystilbene can give only one regioselective product, 1-amino-1-phenyl-2-(4′-methoxyphenyl)ethane (Scheme I).

For the photoamination of the olefins with ammonia, the influences of the arene groups have been mentioned, and the effects of the heterocycle groups are seldom noticed.[8] We have studied the photophysics of 2-styrylthiophenes, and it is found that thiophene moiety can act as electron donor.[9] In this work, we would like to report on the photoaddition of 2-styrylthiophenes **1a**-**1e** with ammonia and that the 2-thienyl group is a more powerful group for the control of the regioselectivity than the *para*-methoxyphenyl group.

Scheme I

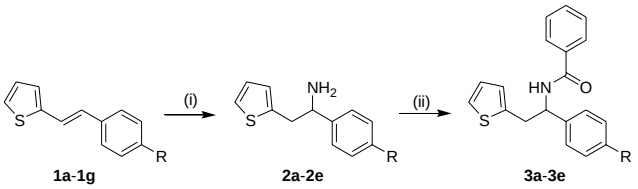


Dedicated to Professor Fa-Ching Chen on the occasion of his ninetieth birthday.

RESULTS AND DISCUSSIONS

Photoamination of 2-styrylthiophenes **1a**-**1e** can give the regioselective products 1-amino-1-aryl-2-(thien-2-yl)-ethanes **2a**-**2e** (Scheme II), and their reaction conditions and results are listed in Table 1. Initially the irradiaton condition in the literature is employed,[4] i.e. NH_3-saturated mix-solvent (CH_3CN:C_6H_6:H_2O = 8:1:1) containing 0.005 M compounds **1** and 0.005 M *p*-DCB was irradiated at 300 nm in a Rayonet photochemical reactor. After irradiation, the reactions show very low conversions (Table 1, Entry 1-5). In order to improve the yield we have tried to change the reaction solvent, the amount of *p*-DCB and the irradiation time.

Scheme II



a: R = OCH_3, **b**: R = CH_3, **c**: R = $CH(CH_3)_2$, **d**: R = H
e: R = F, **f**: R = $N(CH_3)_2$, **g**: R = NO_2

reaction conditions: (i) *hv* 300nm, 2.5eq *p*-DCB, NH_3-saturated CH_3CN, (ii) benzoylchloride, pyridine, CCl_4, ice bath.

It is known that solvent is very influential in a photochemical reaction (Table 1). Compared to the acetonitrile solvent (entry 6), extra water can increase the concentration of dissolved ammonia gas in the media, but the activity of ammonia will be retarded because of the interaction of water and ammonia. The amount of ammonia molecules in NH_3-saturated acetonitrile is enough to react with the 0.005 M reactants and the nucleophility of ammonia in acetonitrile is stronger than that in the mix solvent.

Photoamination reactions can not be carried out in the absence of *p*-DCB. The ratios of the aminated products are increasing with the enhancement of the concentration of *p*-DCB (entry 6-8). This is because more *p*-DCB molecules increase the collision frequency of the reactants. To avoid interfering with the absorbance of the 2-styrylthiophenes, 5 equiv-

Table 1. The Reaction Conditions, Conversions and Yields of the Photoamination of 2-Styrylthiophenes **1a**-**1e**

Entry	Reactant[a]	Solvent[b]	(*p*-DCB/R)	Irrad.time	Conversions	Yields[e]
1	**1a**	mix	1	10	10	50
2	**1b**	mix	1	10	10	72
3	**1c**	mix	1	10	13	62
4	**1d**	mix	1	10	14	83
5	**1e**	mix	1	10	7	80
6	**1c**	CH_3CN	1	2	---	14[c]
7	**1c**	CH_3CN	3	2	---	43[c]
8	**1c**	CH_3CN	5	2	---	67[c]
9	**1c**	CH_3CN	5	0.5	---	14[c]
10	**1c**	CH_3CN	5	1	---	22[c]
11	**1c**	CH_3CN	5	3	---	92[c]
12	**1a**	CH_3CN	5	3	54	91
13	**1a**	CH_3CN	5	5	88	76
14	**1b**	CH_3CN	5	5	100	70
15	**1c**	CH_3CN	5	5	100	47
16	**1d**	CH_3CN	5	3	68	91
17	**1d**	CH_3CN	5	5	100	80
18	**1e**	CH_3CN	5	3	79	71
19	**1e**	CH_3CN	5	5	100	56
20	**1f**	CH_3CN	5	5	0[d]	---
21	**1g**	CH_3CN	5	5	0[d]	---

[a] [**1**] = 0.005 M.
[b] The solvents are saturated with ammonia and the mix-solvent consisted of CH_3CN:C_6H_6:H_2O = 8:1:1.
[c] The ratio of the aminated product estimating by the crude ^1H NMR spectrum.
[d] Only *cis*/*trans*-photoisomerization.
[e] The yields of the product were based on the consumption of the starting material.

alents *p*-DCB are used and less than 5% incident light is absorbed by it. (for example, ε (300 nm) for **1d** = 15164 $M^{-1}cm^{-1}$; ε (300 nm) for *p*-DCB = 120 $M^{-1}cm^{-1}$).

Irradiation time is also one of the factors affecting the reaction yields (entry 8-11). The reaction is clear and only one product is produced within 3-hr of irradiation by estimating the crude H-NMR spectrum. If the irradiation time is increased to 5 hours, some unidentified side products start to appear in the crude H-NMR spectrum. The separated yields of the aminated products also became lower at the longer irradiation time. It means that the products are not stable and are transformed slowly under this irradiation condition.

Finally, the best irradiation condition is chosen: a NH_3-saturated acetonitrile containing 0.005 M compounds **1** and 0.025 M *p*-DCB is irradiated at 300 nm in a Rayonet photochemical reactor. The very high reaction conversions and yields can be achieved at this condition (entry 12-19). But irradiations of 2-(4-dimethylaminostyryl)thiophene **1f** and 2-(4-nitrostyryl)thiophene **1g** undergo only *cis/trans*-isomerization in this condition.

In order to confirm the photoinduced electron transfer between 2-styrylthiophenes and *p*-DCB, one can use the Rehm-Weller equation[10] to estimate the free energy of reaction. (Table 2) The $E_{0,0}$ energy of the compounds **1a**-**1g** has been calculated from the maximum wavelength of absorption and emission, and the oxidation potentials E_{ox} can also be measured in acetonitrile. The free energies of the electron transfer ΔG_{ET} are listed in Table 2. The negative ΔG_{ET} values for the compounds **1a**-**1e** are in accord with the results of the photoamination reactions. The ΔG_{ET} value is also negative for compound **1f**, but there is no photoamination for it. This may be due to the fact that positive charge is localized on the nitrogen atom of the *N*,*N*-dimethylamino group, so that ammonia molecules can not add on the compound **1f**. Another explanation as suggested by one of the referees, could be due to the competition of intramolecular charge transfer for **1f**, since *N*,*N*-dimethylamino group is known to be a good electron donor. For the compound **1g**, the ΔG_{ET} value is positive so that a photoamination reaction can not occur.

For the photoamination products of 2-styrylthiophenes, 1-amino-1-aryl-2-(thien-2-yl)ethanes (**2a**-**2e**), are easily recognized by their NMR spectrum. For example, for the aminated product **2d**, the ^1H NMR peaks for the CH_2 protons of the ethane group are at 3.07 ppm (dd, J = 14.5, 8.0 Hz, 1H) and 3.19 ppm (dd, J = 14.5, 5.1 Hz, 1H), and for the CH proton of the ethane group is at 4.19 ppm (dd, J = 8.0, 5.1 Hz, 1H). The ^{13}C NMR peaks for the CH and CH_2 carbons of the ethane group are at 57.6 and 40.3 ppm, respectively. To determine the regioselectivity, the position of the amino group has been determined by mass spectrum. For the aliphatic amines, the most intense peak will arise from the α-cleavage, and the mass weight of the base peaks for the compounds **2a**-**2e** correspond to the 4-substituted-benzylideneamines which are formed via the α-cleavage of compounds **2a**-**2e**. *N*-(1-Phenyl-2-(thien-2-yl)ethyl)benzamides **3a**-**3e**, the benzoylization of the compounds **2a**-**2e**, also display the corresponding fragmental peaks in the mass spectra to explain the regioselectivity. Finally, the structures and the regioselectivity of the aminated products are confirmed by the X-ray spectrum of the compound **3d** (supporting data).

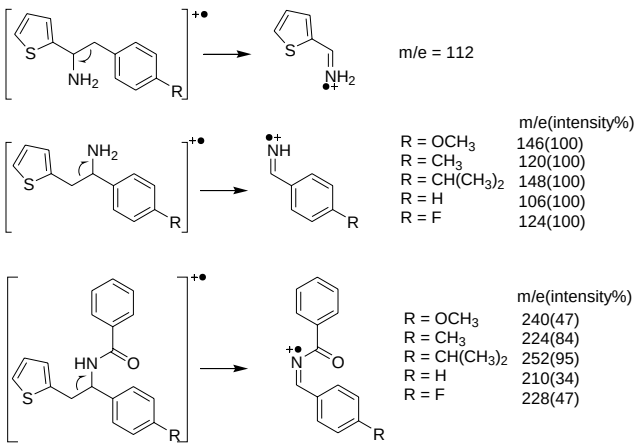
A plausible reaction mechanism for the regioselective photoamination of 2-styrylthiophenes is proposed. Irradiated compounds **1** at 300 nm can produce the singlet excited state (**1***). At the same time, the single electron transfer (SET) occurs from **1*** to *p*-DCB to form the cation radical of the compound **1** ($\mathbf{1}^{+\bullet}$) and the anion radical of *p*-DCB (*p*-$DCB^{-\bullet}$). Then

Table 2. The Spectral Data[a] and ΔG_{ET} Values for the Photoinduced Electron Transfer between 2-Styrylthiophenes **1a**-**1g** and *p*-DCB by Rehm-Weller Equation. Rehm-Weller Eq: $\Delta G_{ET} = E_{ox} - E_{red}$[b] $- E_{0,0} - 0.06$

Reactant	Abs.(nm)	Em.(nm)	$E_{0,0}$(eV)	E_{ox}[c]	ΔG_{ET}
1a	332	388	3.47	1.08	-0.81
1b	325	380	3.54	1.20	-0.75
1c	326	381	3.53	1.23	-0.72
1d	322	377	3.57	1.29	-0.70
1e	321	374	3.59	1.43	-0.58
1f	338	424	3.04	0.64	-0.82
1g	372	588	2.59	1.63	0.62

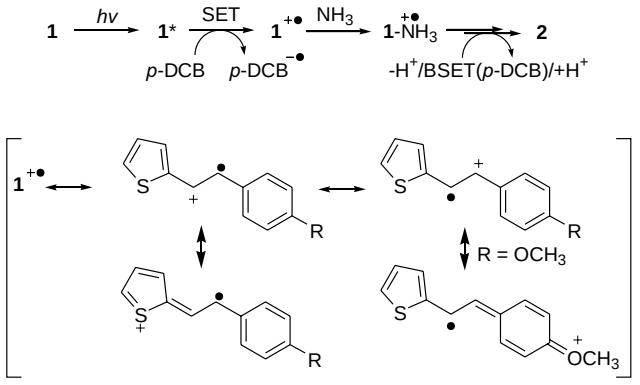
[a] The absorption and emission spectra were measured in acetonitrile.
[b] The reduction potential of *p*-DCB is -1.64 V.
[c] The oxidation potentials vs Ag/AgCl in acetonitrile.

Scheme III



1$^{+\bullet}$ undergoes nucleophilic addition of ammonia, deprotonation, back single electron transfer (BSET) from *p*-DCNB$^{-\bullet}$ and protonation to give the final aminated products **2** (Scheme IV).

Scheme IV



The positive charge of **1**$^{+\bullet}$ can be produced on either site of the ethene part. For the intermediate **1a**$^{+\bullet}$, it has been known that the oxygen atom can localize the cation produced on the benzylic position near the *p*-methoxyphenyl group. However, the sulfur atom on the thiophene group can also stabilize the positive charge on the other side of the ethene, and it even shows a stronger ability of localization of the positive charge. So photoamination of **1a** gives only the product **2a**, and photoaminations of the other reactants **1b**-**1e** give the regioselective products **2b**-**2e**. The 2-thienyl group is stronger than the *p*-methoxyphenyl group in terms of electron donating ability[9] to stabilize the positive charge thus leading to regiospecific amine addition products.

EXPERIMENTAL SECTION

General Methods

^{1}H and ^{13}C NMR spectra were recorded on $CDCl_3$ solutions on Bruker AM-200 WB FT-NMR or Bruker AM-300 WB FT-NMR spectrophotometers. Chemical shifts are reported in parts per million (ppm) relative to TMS as internal standards. Mass spectra were determined with a Finnigan MAT TSCE-46C spectrometer and high resolution mass spectra with a JEOL JMS-HX110 spectrometer. A Rayonet photochemical reactor (300 nm) was used as the irradiation source. UV-Vis absorption spectra were determined with an Hitachi U-2000 spectrometer and fluorescence spectra with an Hitachi F-3000 spectrometer. The redox potentials were determined with an electrochemical analyzer BAS-100, which was equipped with a AgCl/Ag reference electrode, a glassy carbon working electrode and a platinum auxiliary electrode.

The General Procedure for the Preparation of 2-(4′-substitutedstyryl)thiophenes

All reactants, 2-styrylthiophenes **1a**-**1g** were synthesized by Wittig reaction. The mixture of 4-substituted-benzyl chloride (26 mmol) and triphenyl phosphite (31 mmol) was refluxed under nitrogen atmosphere for 4 hours. After refluxing, the reaction was cooled down to room temperature and to which was added 20 mL dry DMF as solvent. Then sodium methoxide (52 mmol) was added quickly into the reaction at 0 °C. After stirring for 10 min, the 2-thiophenecarboxylaldehyde (26 mmol) was added slowly. While the addition was completing, the reaction mixture was kept stirring for several hours at room temperature. Following, the reaction mixture was poured into a lot of ice water, and a white solid appeared. Purification of 2-styrylthiophenes was by recrystallization from ethanol.

The General Procedure for the Photoamination of 2-Styrylthiophenes with Ammonia in the Presence of *p*-Dicyanobenzene

A 100-mL acetonitrile solution containing 0.005 M 2-styrylthiophenes and 0.025 M *p*-DCB in a quartz tube was deaerated by bubbling ammonia gas for a while. The bubbles of ammonia were absorbed by the solution and they were not seen at the beginning. The bubbles were seen gradually and stopped bubbling when the solution was saturated with ammonia. Then the sample was irradiated with a Rayonet Photochemical Reactor at 300 nm. After irradiation, the solution was acidified with 0.1 M hydrochloric acid solution and diluted with water. The aqueous layer was extracted with ethyl

acetate several times to remove the unreacted reactants and *p*-DCB. Then it was basified by 0.1 M sodium hydroxide solution and extracted with ethyl acetate. The ethyl acetate layer was dried by anhydrous $MgSO_4$ and removed in vacuum. The residual mixture was separated by chromatography on silica gel (elute: a mix solution of *n*-hexane and ethyl acetate). The aminated products **2a**-**2e** were gotten. The yields are listed in Table 1, and the spectral data is listed below.

1-Amino-1-(4′-methoxyphenyl)-2-thienylethane (2a)

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.19 (br), 3.11 (dd, *J* = 14.5, 8.0 Hz, 1H), 3.18 (dd, *J* = 14.5, 5.8 Hz, 1H), 3.77 (s, 3H), 4.16 (t, *J* = 6.8 Hz, 1H), 6.76 (d, *J* = 3.6 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.88 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.12 (d, *J* = 5.1 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H).

1-Amino-1-(4′-methylhenyl)-2-thienylethane (2b)

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.34 (s, 3H), 3.06 (dd, *J* = 14.5, 8.6 Hz, 1H), 3.18 (dd, *J* = 14.5, 5.0 Hz, 1H), 4.16 (dd, *J* = 8.6, 5.0 Hz, 1H), 6.81 (d, *J* = 3.5 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H), 7.11-7.15 (m, 3H), 7.25 (d, *J* = 8.1 Hz, 2H). MS (EI, 70 eV) *m/z* 218 (M^++1, 11), 120 ($C_8H_{11}N^+$, 100).

1-Amino-1-(4′-isopropylhenyl)-2-thienylethane (2c)

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.25 (d, *J* = 6.8 Hz, 6H), 2.87 (heptet, *J* = 6.8 Hz, 1H), 3.05 (dd, *J* = 14.5, 9.1 Hz, 1H), 3.18 (dd, *J* = 14.5, 4.7 Hz, 1H), 4.16 (dd, *J* = 9.1, 4.7 Hz, 1H), 6.82 (d, *J* = 3.2 Hz, 1H), 6.92 (dd, *J* = 4.9, 3.2 Hz, 1H), 7.14 (d, *J* = 4.9 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9, 142.5, 141.7, 126.8, 126.5, 126.3, 125.8, 123.9, 57.4, 40.4, 33.7, 24.0. MS (EI, 70 eV) *m/z* 148 ($C_{10}H_{14}N^+$, 100).

1-Amino-1-phenyl-2-thienylethane (2d)

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 3.07 (dd, *J* = 14.5, 8.0 Hz, 1H), 3.19 (dd, *J* = 14.5, 5.1 Hz, 1H), 4.19 (dd, *J* = 8.0, 5.1 Hz, 1H), 6.80 (d, *J* = 3.3 Hz, 1H), 6.91 (dd, *J* = 5.1, 3.3 Hz, 1H), 7.14 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.2-7.4 (m, 5H); ^{13}C-NMR ($CDCl_3$) δ 145.0, 141.3, 128.4, 127.2, 126.8, 126.4, 125.9, 123.9, 57.6, 40.3; MS (EI, 70 eV) *m/z* 204 (M^++1, 62), 106 ($C_7H_8N^+$, 100).

1-Amino-1-(4′-fluorophenyl)-2-thienylethane (2e)

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 3.03 (dd, *J* = 14.4, 8.0 Hz, 1H), 3.14 (dd, *J* = 14.4, 5.2 Hz, 1H), 4.18 (dd, *J* = 8.0, 5.2 Hz, 1H), 6.77 (dd, *J* = 3.4, 0.6 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.99 (dd, *J* = 8.7, 8.7 Hz, 2H), 7.13 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.31 (dd, *J* = 8.4, 5.4 Hz, 2H). MS (EI, 20 eV) *m/z* 222 (M^++1, 22), 124 ($C_7H_7NF^+$, 100).

The General Procedure for the Benzolylation of 1-Amino-1-phenyl-2-thienylethanes

A 10 mL tetrachloromethane containing approx. 30-50 mg isolated 1-amino-1-phenyl-2-thienylethanes (**2a**-**2e**) was kept in an ice bath with stirring. The appropriate amount of benzoyl chloride was added by drops and continued the reaction for 30 minutes. Then pyridine was added dropwise to trap the hydrochloride molecules. The reaction solution was basified and diluted by water then extracted with ethyl acetate several times. The EtOAc layer was dried by anhydrous $MgSO_4$, and the solvent was removed in vacuum. The residual mixture was separated by PTLC chromatography on silica gel (elute: a mixed solution of *n*-hexane and ethyl acetate).

***N*-(2-thiophen-2-yl-1-(4′-methoxyphenyl)ethyl)benzamide (3a)**

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 3.43 (d, *J* = 6.5 Hz, 2H), 3.78 (s, 3H), 5.41 (td, *J* = 8.1, 6.5 Hz, 1H), 6.41 (d, *J* = 8.1 Hz, 1H), 6.73 (dd, *J* = 4.2, 0.8 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.87 (m, 1H), 7.10 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.39-7.48 (m, 3H), 7.71 (dd, *J* = 7.8, 1.4 Hz, 2H). MS (EI, 70 eV) *m/z* 338 (M^++1, 11), 240 ($C_{15}H_{14}NO_2^+$, 47), 105 ($C_7H_5O^+$, 100).

***N*-(2-thiophen-2-yl-1-(4′-methylphenyl)ethyl)benzamide (3b)**

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.32 (s, 3H), 3.43 (d, *J* = 6.5 Hz, 2H), 5.44 (td, *J* = 6.5, 7.6 Hz, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 6.74 (dd, *J* = 3.5, 1.0 Hz, 1H), 6.87 (dd, *J* = 5.1, 3.5 Hz, 1H), 7.10 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.38-7.47 (m, 3H), 7.71 (dd, *J* = 8.2, 1.8 Hz, 2H). MS (EI, 70 eV) *m/z* 322 (M^++1, 1), 224 ($C_{15}H_{14}NO^+$, 84), 105 ($C_7H_5O^+$, 100).

***N*-(2-thiophen-2-yl-1-(4′-isopropylphenyl)ethyl)benzamide (3c)**

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.22 (d, *J* = 6.8 Hz, 6H), 2.88 (heptet, *J* = 6.8 Hz, 1H), 3.44 (d, *J* = 6.6 Hz, 2H), 5.45 (td, *J* = 7.6, 6.6 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 3.4 Hz, 1H), 6.88 (dd, *J* = 5.0, 3.4 Hz, 1H), 7.10 (d, *J* = 5.0 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.34-7.47 (m, 3H), 7.71 (dd, *J* = 8.1, 1.6 Hz, 2H). MS (EI, 20 eV) *m/z* 252 ($C_{17}H_{18}NO^+$, 95), 105 ($C_7H_5O^+$, 100).

***N*-(2-thiophen-2-yl-1-phenylethyl)benzamide (3e)**

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 3.45 (d, *J* = 6.6 Hz,

2H), 5.48 (td, J = 7.5, 6.6 Hz, 1H), 6.53 (d, J = 7.5 Hz, 1H), 6.73 (dd, J = 3.5, 1.0 Hz, 1H), 6.87 (dd, J = 5.1, 3.5 Hz, 1H), 7.10 (dd, J = 5.1, 1.0 Hz, 1H), 7.27-7.48 (m, 8H), 7.72 (dd, J = 7.9, 1.4 Hz, 2H); MS (EI, 70 eV) *m/z* 308 (M^++1, 7), 210 ($C_{14}H_{12}NO^+$, 34), 105 ($C_7H_5O^+$, 100). HRMS Calcd. 307.1031, found 307.1024.

***N*-(2-thiophen-2-yl-1-(4′-fluorophenyl)ethyl)benzamide (3f)**

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 3.41 (d, J = 6.5 Hz, 2H), 5.44 (td, J = 7.3, 6.5 Hz, 1H), 6.50 (d, J = 7.3 Hz, 1H), 6.72 (d, J = 3.5 Hz, 1H), 6.89 (dd, J = 5.1, 3.5 Hz, 1H), 7.00 (td, J = 8.7, 2.1 Hz, 2H), 7.12 (dd, J = 5.1, 1.0 Hz, 1H), 7.25 (dd, J = 8.5, 5.4 Hz, 2H), 7.35-7.49 (m, 3H), 7.71 (dd, J = 8.2, 1.7 Hz, 2H); MS (EI, 20 eV) *m/z* 326 (M^++1, 1), 228 ($C_{13}H_{11}FNO^+$, 47), 105 ($C_7H_5O^+$, 100).

CONCLUSION

A series of 2-styrylthiophenes **1a**-**1g** with various substituents were synthesized. Photochemistry of **1a**-**1g** in the presence of an electron-deficient sensitizer *p*-DCB was studied. The generation of cation radicals of **1a**-**1e** and anion radicals of *p*-DCB is supported by the negative values calculated from the Rehm-Weller equation which is based on the oxidation potentials of **1a**-**1e**. Regioselective photoamination by ammonia is observed to afford 1-amino-1-aryl-2-(thien-2-yl)ethanes (**2a**-**2e**) in relatively good yields. Both *p*-*N*,*N*-dimethylamino (**1f**) and *p*-nitro (**1g**) derivatives are photochemically inactive. A **1g** radical cation is not formed due to the unfavorable oxidation potential and singlet excitation energy.

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