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Photoluminescent and Liquid-Crystalline Properties of Donor–Acceptor-Type 2,5-Diarylthiazoles

Junichi Shikuma,[a, b] Atsunori Mori,*[a, b] Kentaro Masui,[b] Ryuichi Matsuura,[b] Akitoshi Sekiguchi,[b] Haruka Ikegami,[b] Masuki Kawamoto,[b] and Tomiki Ikeda[b]

Abstract: The synthesis of donor–acceptor-type 2,5-diarylthiazoles that bear electron-donating *N*,*N*-dialkylamine and electron-withdrawing cyano groups at the 2- and 5-position, respectively, were carried out with transition-metal-catalyzed C–H arylation reactions developed by us. The compounds were synthesized by the C–H arylation of unsubstituted thiazole at the 2-position with a palladium/copper catalyst in the presence of tetrabutylammonium fluoride (TBAF) as an activator. Further C–H arylation of the 2-arylated thiazole at the 5-position was carried out by the palladium-catalyzed reaction in the presence of silver(I) fluoride to afford the donor–acceptor-type 2,5-diarylthiazoles with *N*,*N*-dialkylamine groups of different chain lengths. The UV/Vis absorption, photoluminescence, and electrochemical behavior were similar regardless of chain length, whereas liquid-crystalline behavior and thermal characteristics were found to be dependent on the alkyl-chain length. The compounds with *N*,*N*-diethylamine or *N*-butyl-*N*-methyl groups showed a stable liquid-crystalline phase over a wide temperature range as well as higher stability to thermal decomposition.

Keywords: arylation · diarylthiazoles · donor–acceptor systems · liquid crystals · photoluminescence

Introduction

Heteroaromatic compounds have attracted considerable attention in the field of advanced materials as well as biologically active compounds.[1] Hence, the development of synthetic methodologies for the facile preparation of these molecules involving construction of the ring structure and introduction of an appropriate substituent at the desired position of the ring is of great interest. We recently showed that the C–H bond at the 2-position of thiazole is substituted with a variety of aryl groups when the synthesis is performed with a catalyst system of Pd^0 and Cu^I in the presence of tetrabutylammonium fluoride (TBAF) as an activator.[2] On the other hand, C–H arylation at the 5-position was shown to take place with a palladium catalyst in the presence of silver(I) fluoride.[3] Hence, 2,5-diarylthiazoles with a variety of aryl substituents can be synthesized in a facile manner under mild conditions compared with related substitution reactions at the C–H bond.[4,5] It was also found that several 2,5-diarylthiazoles showed photoluminescence along with liquid-crystalline characteristics. These results suggest that 2,5-diarylthiazole derivatives are potentially applicable to electroluminescent materials[6] with polarized light emission.[7] Our further studies preliminarily revealed that strong light emission was observed in 2,5-diarylthiazoles with donor–acceptor-type substituents.[2,3a] Herein, we report a systematic study of the characteristics of 2,5-diarylthiazoles that contain a 4-(*N*,*N*-dialkylamino)phenyl group as an electron-donating substituent at the 2-position and a 4-cyanophenyl group as an electron-withdrawing one at the 5-position.

Results and Discussion

Synthesis of the series of 2,5-diarylthiazoles **3a–d** was carried out with tandem C–H substitution reactions of thiazole at the 2- and 5-positions as outlined in Scheme 1. The reaction at the 2-position was performed with thiazole and 4-

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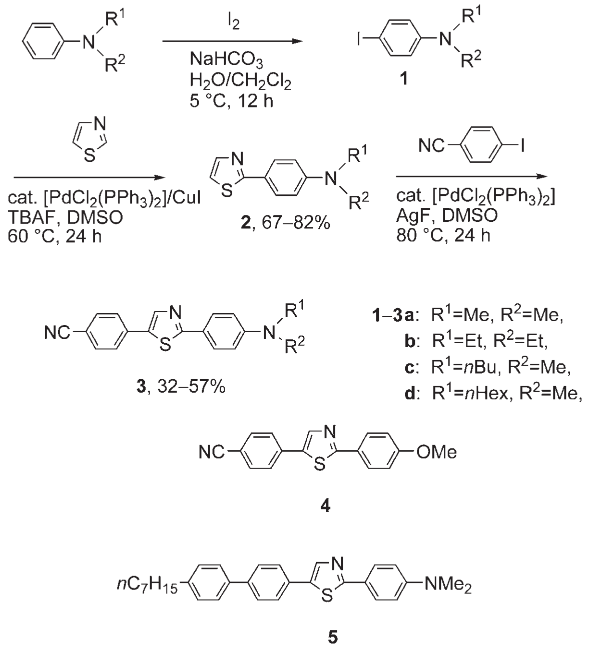
[a] J. Shikuma, Prof. Dr. A. Mori
Department of Chemical Science and Engineering
Kobe University
1-1 Rokkodai, Nada, Kobe 657-8501 (Japan)
Fax: (+81)78-803-6181
E-mail: amori@kobe-u.ac.jp

[b] J. Shikuma, Prof. Dr. A. Mori, K. Masui, R. Matsuura, A. Sekiguchi, H. Ikegami, Dr. M. Kawamoto, Prof. Dr. T. Ikeda
Chemical Resources Laboratory
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama 226-8503 (Japan)



Scheme 1. Synthesis of 2,5-diarylthiazoles. DMSO = dimethyl sulfoxide.

(*N*,*N*-dialkylamino)iodobenzene **1** in the presence of TBAF and catalytic amounts of $[PdCl_2(PPh_3)_2]$/CuI. The reaction proceeded smoothly to afford the 2-arylated thiazole in good to excellent yields. Both solid TBAF·$3H_2O$ and the solution in THF containing 5 % (*w*/*w*) water were similarly effective as an activator; however, in the latter case degassing with three freeze–pump–thaw cycles of the reaction mixture was necessary to achieve high yields.[8] The reaction took place at the 2-position in a highly regioselective manner, and only a trace amount of the 2,5-disubstituted by-product was observed. Formation of 5-arylthiazole was not observed at all. Preparation of **1** was carried out by the iodination of the corresponding *N*,*N*-dialkylaniline.[9] Although complete purification and isolation of **1b–d** were difficult due to continuous decomposition to give dark-blue by-products during chromatography, the crude product obtained was subjected to C–H arylation to give the coupling products **2b–d** in reasonable yields. Introduction of the second aryl group was carried out by the palladium-catalyzed reaction in the presence of AgF as an activator or alternatively by the Miura method,[4a] that is, the reaction with $Pd(OAc)_2$·2PPh_3 in the presence of Cs_2CO_3 at 140 °C. Although both reactions proceeded smoothly to afford the crude product in almost quantitative yields, 2,5-diarylthiazoles **3** partially decomposed during silica-gel column chromatography, which lowered the yield. Although it is difficult to find the reason for this decomposition, the purities of the eluted **3** were found to be acceptable for microanalysis. The related derivatives **4**, which bears the less-electron-donating OMe group, and **5**, which bears an alkylbiphenyl substituent at the 5-position, were prepared in the manner described previously.[2,3a]

Abstract in Japanese:

チアゾール2位および５位でのパラジウム（-銅）触媒を用いるＣＨ結合置換反応を利用することにより2位に電子供与性の置換基、5位に電子求引性の置換基をもつドナーアクセプター型の2,5-ジアリールチアゾールを簡便な手法で合成した。得られた誘導体の分光学的性質、液晶性、電気化学的な酸化還元挙動の評価をおこなった。

The 2,5-diarylthiazoles **3a–d** obtained were subjected to the characterization of spectroscopic properties and liquid-crystalline characteristics. Figure 1 and Table 1 summarize the results of UV/Vis absorption and photoluminescence spectroscopy of the 2,5-diarylthiazoles as dilute solutions in chloroform. The λ_{max} value of the UV/Vis spectrum of **3a** was observed at 398 nm, and the peak of the photoluminescence spectrum was at 488 nm. On the other hand, the UV/

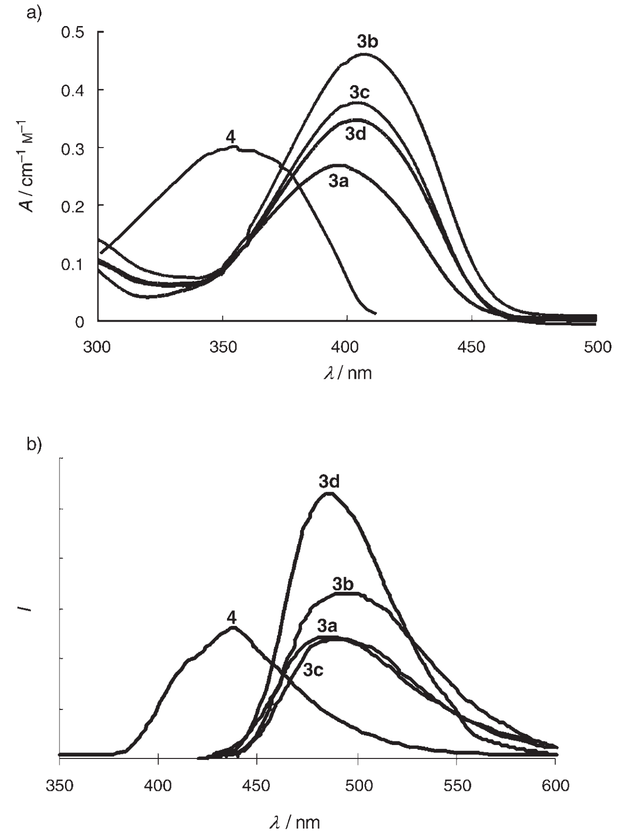


Figure 1. a) UV/Vis and b) photoluminescence spectra of **3a–d** and **4**.

Table 1. Spectroscopic properties of 2,5-diarylthiazoles.[a]

2,5-Diaryl-thiazole	UV/Vis λ_{max}[mm]	ε [$M^{-1}m^{-1}$]	Excitation λ_{max} [nm]	Emission λ_{max} [nm]	Quantum yield Φ
3a	398	26900	395	488	0.37
3b	407	46100	405	493	0.60
3c	404	37700	405	492	0.55
3d	404	34800	406	486	0.74
4	350	30200	346	462	0.27
5	376	38200	374	462	0.49

[a] See Experimental Section (General).

Vis and photoluminescence spectra of **4** with the 4-methoxy group showed values at 350 nm and 462 nm, respectively. The results suggest that the presence of the strongly electron-donating NMe_2 group brought about a larger red shift in the UV/Vis and photoluminescence spectra than for the less-electron-donating OMe group. Furthermore, a higher quantum yield was observed for **3a–d**, which would also be the result of the donor–acceptor effect. By contrast, the length of the alkyl chain on the nitrogen atom influenced the wavelength of the UV/Vis and photoluminescence peaks to a lesser extent (Table 1).

Table 2 shows the results of cyclic voltammetry (CV) for **3a–d**, **4**, and **5**. The oxidation peaks of **3a–d** observed at about 0.5 V show the effect of the *N*,*N*-dialkylamine group, whereas the oxidation peak of **4** was observed at 1.15 V. The results suggest that the strongly electron-donating characteristics of the dialkylamine group lower the oxidation potential. On the other hand, reduction peaks of **3a–d** were observed at about 2.2 V, and no peak was seen for **5**, which did not contain electron-withdrawing substituents. Therefore, it seems that 2,5-diarylthiazoles must contain an electron-withdrawing substituent on the aryl group of the 5-position to show the reduction peak.

Table 2. Electrochemical redox behavior of 2,5-diarylthiazoles by cyclic voltammetry.[a]

2,5-Diarylthiazole	E_{pa} ($E_{1/2}$) [V]	E_{pc} [V]
3a	0.50 (0.47), 1.13 (1.08)	−2.17
3b	0.49 (0.46), 1.13	−2.18
3c	0.50 (0.47), 1.14	−2.13
3d	0.47 (0.45), 1.11	−2.19
4	1.15	−2.17
5	0.47 (0.43), 0.95 (0.90)	not observed

[a] Cyclic voltammograms were recorded in solutions of Et_4NBF_4 (0.1 M) in acetonitrile. Scanning rate was 0.1 Vs^{-1}. Ag^+/Ag was the reference electrode. E_{pa} = peak anode potential, E_{pc} = peak cathode potential.

Table 3. Thermal characteristics of 2,5-diarylthiazoles.

2,5-Diaryl-thiazole	DSC T [°C][a]	TGA T_d [°C][b]
3a	I→S: 204.3 (11.2), S→Cr: 188.0 (4.0)	297, 196,[c] 206[d]
3b	I→S: 182.8 (6.7), S→Cr: 131.5 (17.6)	306
3c	I→S: 180.4 (4.8), S→Cr: 89.2 (12.4)	300
3d	I→S: 165.5 (4.5), S→Cr: 82.3 (9.2)	–
4	I→N: 225 (0.04), N→Cr: 151 (6.7)	–
5	I→N: 258 (0.26), N→Cr: 145 (3.5)	–

[a] Phase-transition temperatures of liquid-crystalline (S = smectic, N = nematic) to isotropic (I) phase and crystal (Cr) to liquid-crystalline phase by differential scanning calorimetry (DSC). The ΔH value (kcal mol^{-1}) of each phase transition is given in parentheses. [b] Temperature at which a weight loss of 5% was observed by thermogravimetric analysis (TGA) under nitrogen atmosphere. [c] Temperature at which 1% weight loss occurred over 3 h. [d] Temperature at which 2.2% weight loss occurred over 3 h.

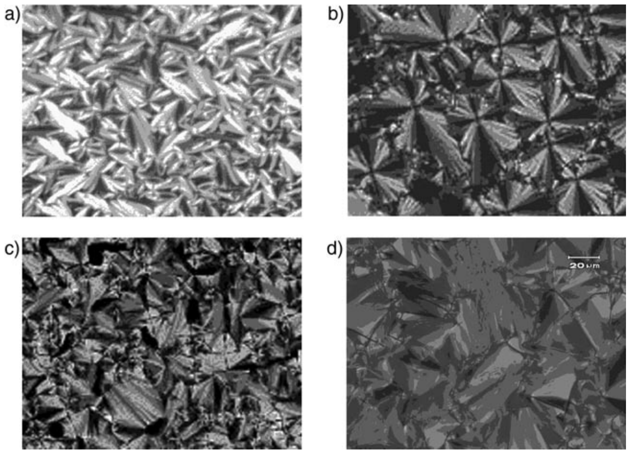


Figure 2. Polarized optical microscopy images of **3a–d**. a) **3a** at 210 °C, b) **3b** at 170 °C, c) **3c** at 180 °C, d) **3d** at 94 °C.

The thermal characteristics of **3a–d**, **4**, and **5** are summarized in Table 3. All the compounds exhibited liquid-crystalline characteristics over a wide range of temperature. Figure 2 shows the polarized optical microscopy images at the specified temperatures, which also support the presence of the liquid-crystalline phase. By contrast, the spectroscopic properties of **3a–d** exhibited little difference; however, the structure of the *N*,*N*-dialkylamine moiety had a remarkable influence on the thermal characteristics observed. Furthermore, the DSC thermograms of **3** versus **4** and **5** exhibited differences in the ΔH of the transition of the liquid-crystalline to the isotropic phase, showing larger values for **3** (4.5–11.2 kcal mol^{-1}) than for **4** and **5** (0.04 and 0.26 kcal mol^{-1}, respectively) (Table 3). These results suggest that donor–acceptor-type 2,5-diarylthiazoles show the smectic phase, whereas **4** and **5** are nematic liquid crystals. The polarized optical microscopy images of **3a–d** (Figure 2), which show characteristic batnet structures, also support the formation of the smectic liquid-crystalline phase, while those of **4** and **5** indicate the nematic phase.[1c] This remarkable difference could be explained by the intermolecular interaction between donor and acceptor substituent moieties of 2,5-diarylthiazoles, that is, the *N*,*N*-dialkylaminophenyl and 4-cyanophenyl groups. The interaction would bring about a definite layer width leading to the smectic liquid crystal. On the other hand, 2,5-diarylthiazole **5**, which does not contain acceptor substituents, has little intermolecular interaction, resulting in the nematic phase.[1c] Furthermore, the donor effect of the methoxy group of **4** was not found to be strong enough to form a donor–acceptor complex with a neighboring molecule, thereby also leading to the nematic phase. By contrast, the chain length of the *N*,*N*-dialkylamine group of **3** did not affect the UV/Vis absorption and photoluminescence spectra much; the temperature range of the liquid-crystalline phase was expanded as the chain length of the *N*-alkyl group became longer. Indeed, **3d** exhibited the smectic phase at 82–166 °C, as opposed to **3a**, whose corresponding range was 188–204 °C. Notably, thiazole derivatives show liquid-crystalline characteristics over a wide range of temperatures. Although the related heteroaromatic compound oxadiazole, which bears the same substituents as **5** (145–258 °C), also exhibited a liquid-crystal phase, the temperature range of the nematic phase was only 138–143 °C.[7a] Accordingly, the stable liquid-crystalline characteristics of 2,5-diarylthiazoles are potentially advantageous for the design of electroluminescent devices with polarized light emission.

2,5-Diarylthiazoles **3a–c** also showed different thermal stabilities. TGA of **3** showed that a weight loss of 5 % occurred at a temperature of around 300 °C (Table 3). However, for **3a**, a 1 % weight loss was observed at 196 °C over 3 h and a 2.2 % loss at 206 °C over 3 h. On the other hand, such weight loss was not observed in the analyses of **3b** and **3c**. Thus, donor–acceptor-type 2,5-diarylthiazoles with longer alkyl chains are thermally stabilized relative to the corresponding dimethylamine derivative.

We next envisaged the production of polarized light emission by forming a preliminary single-layered electroluminescent device. Compound **3c** was introduced onto the glass plates (2-μm width) of an indium tin oxide (ITO) electrode at the temperature range of the liquid-crystalline phase. However, light emission was hardly observed due to the thickness of liquid-crystalline **3c**. The attempted electroluminescence suggests that formation of a thin film of **3** to drive the device at a lower voltage, which would be realized by polymeric materials bearing the 2,5-diarylthiazole moiety, is necessary.

Conclusions

We have shown that C–H substitution reactions of five-membered heteroaromatic compounds take place under mild conditions. By utilizing the reactions, 2,5-diarylthiazoles that bear various substituents on the aromatic rings were synthesized under mild conditions from unsubstituted thiazole in a facile manner. Donor–acceptor-type 2,5-diarylthiazoles were found to show strong photoluminescence regardless of the difference in the chain length of the alkyl group on the nitrogen atom, whereas the chain length significantly influenced the stability of the liquid-crystalline characteristics. As 2,5-diarylthiazoles attract remarkable interest in the design of advanced organic materials, the mild and facile C–H substitution reactions would be a powerful tool for the combinatorial preparation of a wide variety of derivatives.

Experimental Section

General

Melting points are uncorrected. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded with a Varian Mercury 300 spectrometer. Chemical shifts are expressed in ppm relative to tetramethylsilane (0 ppm for ^{1}H) or $CDCl_3$ (77 ppm for ^{13}C) as an internal standard. UV/Vis and photoluminescence spectra were recorded as 1×10^{-5} M and 1×10^{-6} M solutions in chloroform, respectively. Quantum yields Φ were estimated by comparison of standard solution of quinine sulfate (1.0 M, $\Phi=0.546$). CV was performed on an ALS/chi Model 600 A electrochemical analyzer in a solution of tetraethylammonium tetrafluoroborate (0.1 M) in acetonitrile at a scan rate of 100 mV s^{-1}. Measurements were carried out with a platinum disk (1.6-mm diameter) as the working electrode. Platinum wire was used as the counterelectrode. Prior to each series of measurement, the cell was deoxygenated with argon. Liquid-crystalline and phase-transition behavior were examined on an Olympus Model BH-2 polarizing microscope equipped with Mettler hot stage Models FP-90 and FP-82. Thermotropic properties of the liquid-crystalline compounds were determined with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC 220C) at a heating rate of 3 °C min^{-1}. TGA was performed with a Seiko Instrument TG/DTA-220. Measurements were carried out under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}.

Materials: The synthesis of **3a** was performed in the manner reported previously.[2] Preparation of **1b–d** was carried out in a similar manner to the synthesis of **1a**. Although aryl iodides **1a–d** are deep-blue in color and were found to be difficult to purify to analytical grade, these were employed for the C–H coupling reaction without further purification. TBAF was used as a solution (1 M) in THF containing H_2O (5 % *w*/*w*), purchased from Aldrich Co. Ltd., or TBAF·3H_2O (solid) from Tokyo Kasei Inc. DMSO was distilled from $CaSO_4$ and stored over 4-Å molecular sieves or purchased from Kanto Chemicals Co. Ltd. as anhydrous and used without further purification. Other chemicals were purchased and used as such.

Syntheses

2c: [$PdCl_2(PPh_3)_2$] (84.2 mg, 0.12 mmol), CuI (15.2 mg, 0.08 mmol), and **4c** (1.16 g, 4.0 mol) were added to a 100-mL Schlenk tube. The mixture was dissolved in DMSO (3 mL) under an argon atmosphere. Compound **1** (568 μL, 8.0 mmol) and TBAF (8.0 mL, 8.0 mmol; 1 M solution in THF, water content 5 wt %, Aldrich) were successively added to the solution. The resulting solution was degassed with three freeze–pump–thaw cycles, heated in an oil bath (60 °C), and stirred for 24 h. Upon cooling to room temperature, the solution was diluted by ethyl acetate and poured into water. The two phases were separated. The aqueous layer was extracted with ethyl acetate. The combined extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate as eluent) to give **2c** (297 mg, 82 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.95$ (t, $J=7.5$ Hz, 3 H), 1.30–1.42 (m, 2 H), 1.56–1.61 (m, 2 H), 3.00 (s, 3 H), 3.37 (t, $J=7.5$ Hz, 2 H), 6.69 (d, $J=9.0$ Hz, 2 H), 7.15 (d, $J=3.3$ Hz, 1 H), 7.74 (d, $J=3.3$ Hz, 1 H), 7.81 ppm (d, $J=9.0$ Hz, 2 H). Other 2-arylthiazoles were synthesized similarly.

2b: The product contained a trace amount of inseparable impurity after chlormatography on silica gel. The crude material was used for the coupling reaction without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.20$ (t, $J=7.2$ Hz, 6 H), 3.41 (q, $J=7.2$ Hz, 4 H), 6.68 (d, $J=9.0$ Hz, 2 H), 7.15 (d, $J=3.3$ Hz, 1 H), 7.74 (d, $J=3.3$ Hz, 1 H), 7.80 ppm (d, $J=9.0$ Hz, 2 H).

2d: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.90$ (t, $J=6.3$ Hz, 3 H), 1.21–1.39 (m, 6 H), 1.51–1.61 (m, 2 H), 3.00 (s, 3 H), 3.36 (d, $J=7.5$ Hz, 2 H), 6.68 (d, $J=9.0$ Hz, 2 H), 7.16 (d, $J=3.3$ Hz, 1 H), 7.75 (d, $J=3.3$ Hz, 1 H), 7.81 ppm (d, $J=8.7$ Hz, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=13.9$, 22.4, 26.51, 26.54, 31.5, 38.1, 52.2, 111.2, 116.1, 121.1, 127.6, 142.8, 150.2, 169.1 ppm.

3b: The reaction was carried out by a procedure similar to that reported by Miura and co-workers[4a] with $Pd(OAc)_2$·2PPh_3 (10 mol %) and $CsCO_3$ in *N*,*N*-dimethylformamide (DMF) at 140 °C. IR (KBr): $\tilde{\nu}=2971$, 2928, 2359, 2220, 1601 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.20$ (t, $J=6.9$ Hz, 6 H), 3.41 (q, $J=6.9$ Hz, 4 H), 6.68 (d, $J=8.3$ Hz, 2 H), 7.62 (s, 4 H), 7.72 (d, $J=8.3$ Hz, 2 H), 7.98 ppm (s, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta=12.5$, 44.5, 110.5, 111.1, 118.7, 120.3, 126.3, 128.0, 132.7, 134.1, 136.4, 140.6, 149.3, 170.1 ppm; elemental analysis: calcd (%) for $C_{20}H_{21}N_3S$: C 72.04, H 5.74, N 12.60, S 9.62; found: C 72.07, H 5.92, N 12.58, S 9.42.

C–H arylation reaction in the presence of AgF as an activator: [$PdCl_2(PPh_3)_2$] (70.2 mg, 0.1 mmol), **2d** (551 mg, 2.0 mmol), and 4-iodobenzonitrile (916 mg, 4.0 mmol) were added to a 25-mL Schlenk tube. The mixture was dissolved in DMSO (10 mL) under an argon atmosphere. AgF (257 mg, 2.0 mmol) was added to the mixture, which was heated at 80 °C for 5 h. More AgF (2×(193 mg, 1.5 mmol)) was added after the mixture was stirred for 5 and 10 h, respectively. Stirring was continued for 24 h, then the mixture was passed through a celite pad, which was successively washed with chloroform. The filtrate was washed with water, and the aqueous layer was extracted with chloroform. The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid. The solid was purified by column chromatography on silica gel (dichloromethane/ethyl acetate as eluent) to give **3d** (429 mg, 57%).

3c: IR (KBr): $\tilde{\nu}=2957$, 2920, 2870, 2365, 2218, 1601 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=0.95$ (t, $J=7.5$ Hz, 3H), 1.29–1.41 (m, 2H), 1.52–1.62 (m, 2H), 2.98 (s, 3H), 3.35 (t, $J=7.5$ Hz, 2H), 6.65 (d, $J=9.0$ Hz, 2H), 7.58 (s, 4H), 7.76 (d, $J=9.0$ Hz, 2H), 7.96 ppm (s, 1H); ^{13}C NMR (75.5 MHz, CDCl$_3$): $\delta=13.9$, 20.2, 28.9, 38.2, 52.1, 110.4, 111.3, 118.6, 120.5, 126.2, 127.8, 132.6, 140.5, 150.7, 169.9 ppm; elemental analysis: calcd (%) for $C_{21}H_{21}N_3S$: C 72.59, H 6.09, N 12.09, S 9.23; found: C 72.58, H 6.01, N 12.02, S 9.11.

3d: IR (KBr): $\tilde{\nu}=2928$, 2224, 1601, 1414, 812 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=0.89$ (t, $J=6.3$ Hz, 3H), 1.21–1.39 (m, 6H), 1.52–1.66 (m, 2H), 3.02 (s, 3H), 3.38 (t, $J=6.6$ Hz, 2H), 7.11 (d, $J=8.7$ Hz, 2H), 7.65 (s, 4H), 7.83 ppm (d, $J=8.7$ Hz, 2H), 8.02 (s, 1H); ^{13}C NMR (75.5 MHz, CDCl$_3$): $\delta=14.0$, 22.6, 26.67, 26.71, 31.6, 38.3, 52.4, 110.5, 111.3, 118.7, 120.6, 126.4, 127.9, 132.7, 134.2, 136.4, 140.6, 150.8, 170.0 ppm; MS (EI): *m/z* calcd: 375.1769; found: 375.1779.

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