Synthesis of 2-Styrylbenzoxazole Derivatives by the Reaction of Styrylphenolic Schiff Bases with Thianthrene Cation Radical

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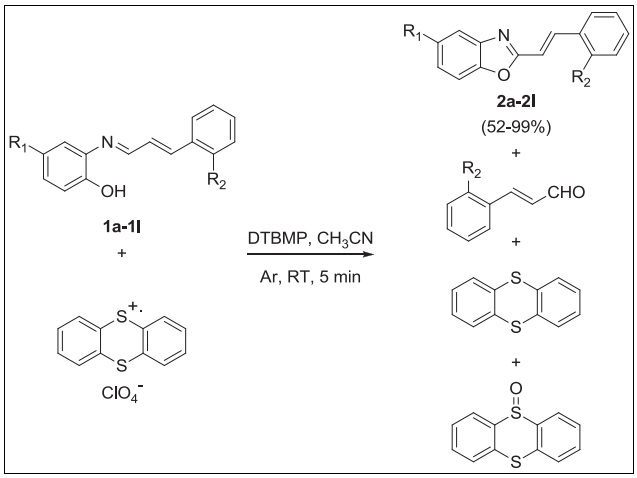

A simple and fast preparative method of 2-styrylbenzoxazoles by oxidative intramolecular cyclization of styrylphenolic Schiff bases with thianthrene cation ($Th^{+\cdot}ClO_4^-$) is described. The oxidative cyclization of Schiff bases in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) gives 2-styrylbenzoxazole derivatives in better yields than those in the absence of DTBMP.

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INTRODUCTION

2-Styrylbenzoxazoles have attracted interests for their fluorescent and biological significance. For instance, 2-styrylbenzoxazoles have been utilized as invisible markings and brightening agents for polymeric organic materials such as synthetic fibres and resin masses [1], and as potent drugs [2]. Because of their diverse applications in industry, many methods are documented in the literature for the synthesis of 2-styrylbenzoxazoles, including the condensation of 2-aminophenol and carboxylic acid [3], cyclization of corresponding Schiff base with an oxidant [4], Beckmann rearrangement of oximes [5], condensation of 2-methylbenzoxazole with aldehydes [6], and *o*-dihalobenzene and primary amides [7]. However, many of these methods suffer from drawbacks due to long reaction times and high temperatures. Herein, we have employed thianthrene cation radical perchlorate ($Th^{+\cdot}ClO_4^-$) as an oxidant [8] by which 2-styrylbenzoxazole is efficiently obtained from styrylphenolic Schiff bases **1** under mild conditions.

RESULTS AND DISCUSSION

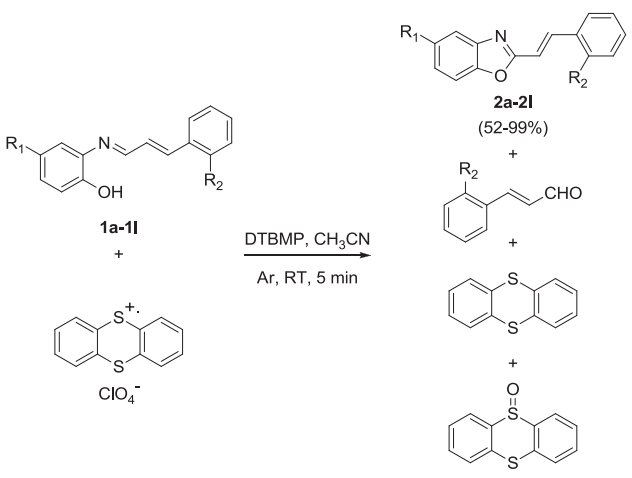
The reaction under argon of styrylphenolic Schiff base **1** and $Th^{+\cdot}ClO_4^-$ (2 equiv) at room temperature in acetonitrile with 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) afforded 2-styrylbenzoxazole **2**, corresponding cinnamaldehyde, thianthrene (Th), and its 5-oxide (ThO) as shown in Scheme 1.

Although the reactions were complete generally within 5–10 min, the reaction was done after further stirring overnight by extracting the neutralized aqueous solution with dichloromethane. Each product was analysed quantitatively by gas chromatography (GC). Considering the general reaction conditions reported in the literature, that is, several hours of heating (80–100°C), the very fast reactions of **1** and $Th^{+\cdot}ClO_4^-$ at room temperature in good yields (52–99%) are noteworthy. The other products observed in these reactions were Th as a redox partner and ThO. In all of the reactions, formation of ThO is not related to the main reaction but stems from the hydrolysis of $Th^{+\cdot}ClO_4^-$ due to either adventitious water or water added during the work-up procedure.

The results from 12 reactions are shown in Table 1. The addition of DTBMP was required to prevent aldehyde formation in all cases and accordingly to make higher yields of 2-styrylbenzoxazole products.

In the absence of DTBMP, the reactions were sluggish with much lower yields (16–47%) as shown in Table 2. In these reactions, formation of aldehydes in appreciable

Scheme 1



amounts is obviously caused by the hydrolysis of substrates by liberated acid ($HClO_4$).

The oxidative intramolecular cyclization reaction of 2-styrylphenolic Schiff bases has shown that the use of more electron rich alkenyl groups gave lower yields, that is, when R_2 was electron-donating group.

According to our previous studies [8], we assumed that phenoxyl radical might be the first formed intermediate by the reaction of **1** with $Th^{+\cdot}ClO_4^-$. The intermediate phenoxyl radical with an electron-donating group might react intramolecularly with adjacent double bond, C═N group and α-styryl carbon.

CONCLUSIONS

A mild and convenient method for the synthesis of 2-styrylbenzoxazole derivatives has been described. The reaction proceeded in good yields by the oxidative intramolecular cyclization of styrylphenolic Schiff bases **1** with thianthrene cation radical perchlorate ($Th^{+\cdot}ClO_4^-$) in the presence of DTBMP in acetonitrile.

EXPERIMENTAL

Acetonitrile was purified by distillation over phosphorus pentoxide under argon prior to use. Thianthrene was recrystallized

Table 1

Yield[a] (%) of products in the reactions of thianthrene cation radical perchlorate ($Th^{+\cdot}ClO_4^-$) with **1** in the presence of DTBMP.

Compound	R_1	R_2	**2**	Th	DTBMP	ThO
a	H	H	85	97	90	3
b	CH_3	H	69	97	89	3
c	*t*-Butyl	H	52	98	88	2
d	Cl	H	95	99	85	1
e	H	NO_2	99	97	90	3
f	CH_3	NO_2	90	97	84	3
g	*t*-Butyl	NO_2	70	98	86	2
h	Cl	NO_2	84	96	85	4
i	H	OCH_3	61	98	86	2
j	CH_3	OCH_3	58	97	83	3
k	*t*-Butyl	OCH_3	54	96	80	4
l	Cl	OCH_3	66	96	82	4

[a]The yield was quantitatively determined by GC.

Table 2

Yield[a] (%) of products in the reactions of thianthrene cation radical perchlorate ($Th^{+\cdot}ClO_4^-$) with **1** in the absence of DTBMP.

Compound	R_1	R_2	**1**	**2**	Th	Aldehyde	ThO
a	H	H	20	34	81	24	1
b	CH_3	H	20	22	84	20	2
e	H	NO_2	12[b]	47	92	24	0
i	H	OCH_3	0	26	77	24	0
j	CH_3	OCH_3	0	16	85	16	1
k	*t*-Butyl	OCH_3	0	18	84	24	1
l	Cl	OCH_3	0	24	83	16	2

[a]The yield was quantitatively determined by GC.
[b]2-Aminophenol.

twice from acetone. Aldehydes and aminophenols were used without further purification.

Thianthrene cation radical perchlorate ($Th^{+\cdot}ClO_4$). The known procedure [9] was adopted as follows. To a solution of perchloric acid (70%, 0.60 mL) in acetic anhydride (33 mL) was added a solution of thianthrene (1.0 g, 4.6 mmol) in carbon tetrachloride (66 mL). The reaction mixture was then allowed to stand for 24 h in the dark at room temperature. Dark purple coloured crystals were formed and were collected by filtration and washed with carbon tetrachloride until the filtrate was colourless. The crystals were then dried in a flask under vacuum. The product (1.2 g, 3.9 mol, 84%) was dried under vacuum for short period before use.

General procedure for the preparation of styrylphenolic Schiff bases (1). To a stirred solution of 2-aminophenol (20 mmol) in ethanol (20 mL) was added dropwise a solution of *trans*-cinnamaldehyde (20 mmol) in ethanol (20 mL) at room temperature. After stirring for 2 h, the compound was obtained as yellow crystals (ethanol).

2-[(3-Phenyl-2-propenylidene)amino]phenol (1a). Yield; 76%, mp 90–92°C (lit. mp 92°C [10]). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (d, J = 7.8 Hz, 1H, N=CH), 7.55 (d, J = 8.1 Hz, 1H, Ar-H), 7.42–7.38 (m, 5H, Ar-H), 7.26–7.13 (m, 4H, Ar-H, OH), 7.02 (d, J = 8.1 Hz, 1H, CH), 6.90 (t, J = 7.7 Hz. 1H, CH).

4-Methyl-2-[(3-phenyl-2-propenylidene)amino]phenol (1b). Yield; 74%, mp 76–77°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (d, J = 7.7 Hz, 1H, N=CH), 7.57–7.35 (m, 5H, Ar-H, CH), 7.27–6.90 (m, 6H, Ar-H, CH, OH), 2.32 (s, 3H, CH_3). *Anal*. Calcd for $C_{16}H_{15}NO$: C, 81.01; H, 6.33; N, 5.91. Found: C, 80.88; H, 6.46; N, 5.89.

***4-tert*-Butyl-2-[(3-phenyl-2-propenylidene)amino]phenol (1c)**. Yield; 76%, mp 107–108°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (d, J = 8.2 Hz, 1H, N=CH), 7.58–7.38 (m, 5H, Ar-H, CH), 7.27–7.09 (m, 5H, Ar-H, CH), 6.95 (d, J = 8.2 Hz, 1H, Ar-H), 1.36 (s, 9H, CH_3). *Anal*. Calcd for $C_{19}H_{21}NO$: C, 81.72; H, 7.53; N, 5.02. Found: C, 81.23; H, 7.66; N, 4.83.

4-Chloro-2-[(3-phenyl-2-propenylidene)amino]phenol (1d). Yield; 63%, mp 105–107°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.35 (s, 1H, OH), 8.43 (d, J = 8.8 Hz, 1H, N=CH), 7.64 (m, 2H, Ar-H, CH), 7.45–7.33 (m, 4H, Ar-H, CH), 7.15 (d, J = 8.8 Hz, 1H, Ar-H), 7.12–7.09 (m, 1H, Ar-H), 7.06 (d, J = 8.5 Hz, 1H, Ar-H), 6.87 (d, J = 8.5 Hz, 1H, Ar-H). *Anal*. Calcd for $C_{15}H_{12}ClNO$: C, 70.04; H, 4.67; N, 5.45. Found: C, 69.64; H, 4.64; N, 5.28.

2-[[3-(2-Nitrophenyl)-2-propenylidene]amino]phenol (1e). Yield; 90%, mp 126–128°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.10 (s, 1H, OH), 8.54 (d, J = 8.8 Hz, 1H, N=CH), 8.03 (d, J = 8.1 Hz, 1H, Ar-H), 7.99 (d, J = 7.9 Hz, 1H, Ar-H), 7.76 (dd, J = 8.1 Hz, 7.8 Hz, 1H, Ar-H), 7.63 (dd, J = 7.9 Hz, 7.8 Hz, 1H, Ar-H), 7.60 (d, J = 15.8 Hz, 1H, CH), 7.15 (dd, J = 15.8 Hz, 8.8 Hz, 1H, CH), 7.11 (d, J = 7.7 Hz, 1H, Ar-H), 7.03 (dd, J = 8.1 Hz, 7.6 Hz, 1H, Ar-H), 6.88 (d, J = 8.1 Hz, 1H, Ar-H), 6.80 (dd, J = 7.7 Hz, 7.6 Hz, 1H, Ar-H).

4-Methyl-2-[[3-(2-nitrophenyl)-2-propenylidene]amino]phenol (1f). Yield; 93%, mp 151–153°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.85 (s, 1H, OH), 8.54 (d, J = 8.8 Hz, 1H, N=CH), 8.03 (d, J = 8.1 Hz, 1H, Ar-H), 8.00 (d, J = 7.9 Hz, 1H, Ar-H), 7.76 (dd, J = 8.1 Hz, 7.8 Hz, 1H, Ar-H), 7.63 (dd, J = 7.9 Hz, 7.8 Hz, 1H, Ar-H), 7.56 (d, J = 15.8 Hz, 1H, CH), 7.20–7.12 (dd, J = 15.8 Hz, 8.8 Hz, 1H, CH), 6.96 (s, 1H, Ar-H), 6.86 (d, J = 8.1 Hz, 1H, Ar-H), 6.76 (d, J = 8.1 Hz, 1H, Ar-H), 2.20 (s, 3H, CH_3). *Anal*. Calcd for $C_{16}H_{14}N_2O_3$: C, 68.03; H, 4.96; N, 9.93. Found: C, 67.94; H, 4.96; N, 9.82.

4-t-Butyl-2-[[3-(2-nitrophenyl)-2-propenylidene]amino]phenol (1g). Yield; 72%, yellow crystal with mp 147–149°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.89 (s, 1H, OH), 8.63 (d, J = 8.8 Hz, 1H, N=CH), 8.02 (d, J = 8.1 Hz, 1H, Ar-H), 7.99 (d, J = 7.7 Hz, 1H, Ar-H), 7.77 (dd, J = 7.7 Hz, 7.4 Hz, 1H, Ar-H), 7.62 (dd, J = 8.1 Hz, 7.4 Hz, 1H, Ar-H), 7.60 (d, J = 15.8 Hz, 1H, CH), 7.21–7.14 (dd, J = 15.8 Hz, 8.8 Hz, 1H, CH), 7.13 (s, 1H, Ar-H), 7.09 (d, J = 8.4 Hz, 1H, Ar-H), 6.80 (d, J =8.4 Hz, 1H, Ar-H), 1.26 (s, 9H, CH_3).

4-Chloro-2-[[3-(2-nitrophenyl)-2-propenylidene]amino]phenol (1h). Yield; 87%, mp 184–185°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.44 (s, 1H, OH), 8.55 (d, J = 8.8 Hz, 1H, N=CH), 8.04–7.99 (dd, J = 8.1Hz, 7.7 Hz, 2H, Ar-H), 7.77 (dd, J = 7.6 Hz, 7.5 Hz, 1H, Ar-H), 7.62 (dd, J = 8.1 Hz, 7.5 Hz, 1H, Ar-H), 7.65–7.59 (d, J = 15.8 Hz, 1H, CH), 7.20–7.11 (m, 2H, Ar-H, CH), 7.09 (d, J = 8.6 Hz, 1H, Ar-H), 6.87 (d, J = 8.6 Hz, 1H, Ar-H). *Anal*. Calcd for $C_{15}H_{11}ClN_2O_3$: C, 59.60; H, 3.64; N, 9.27. Found: C, 59.34; H, 3.62; N, 9.06.

2-[[3-(2-Methoxyphenyl)-2-propenylidene]amino]phenol (1i). Yield; 81%, mp 76–78°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.92 (s, 1H, OH), 8.45 (d, J = 8.9 Hz, 1H, N=CH), 7.66 (d, J = 7.7 Hz, 1H, Ar-H), 7.51 (d, J = 16.1 Hz, 1H, CH), 7.36 (t, J = 7.7 Hz, 1H, Ar-H), 7.19 (dd, J = 16.1 Hz, 8.9 Hz, 1H, CH), 7.11–6.99 (m, 4H, Ar-H), 6.85–6.78 (m, 2H, Ar-H), 3.86 (s, 3H, OCH_3). *Anal*. Calcd for $C_{16}H_{15}NO_2$: C, 75.89; H, 5.93; N, 5.53. Found: C, 75.60; H, 5.99; N, 5.41.

4-Methyl-2-[[3-(2-methoxyphenyl)-2-propenylidene]amino]phenol (1j). Yield; 96%, mp 109–110°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.67 (s, 1H, OH), 8.45 (d, J = 8.9 Hz, 1H, N=CH), 7.65 (d, J = 7.7 Hz, 1H, Ar-H), 7.50 (d, J = 16.1 Hz, 1H, CH), 7.35 (dd, J = 7.7 Hz, 7.8 Hz, 1H, Ar-H), 7.15 (dd, J = 16.1 Hz, 8.9 Hz, 1H, CH), 7.18–7.06 (m, 1H, Ar-H), 6.99 (t, J = 7.8 Hz, 1H, Ar-H), 6.92 (s, 1H, Ar-H), 6.83 (d, J = 8.1 Hz, 1H, Ar-H), 6.72 (d, J = 8.1 Hz, 1H, Ar-H), 3.86 (s, 3H, OCH_3), 2.19 (s, 3H, CH_3). *Anal*. Calcd for $C_{17}H_{17}NO_2$: C, 76.40; H, 6.37; N, 5.24. Found: C, 76.27; H, 6.51; N, 5.13.

***4-tert*-Butyl-2-[[3-(2-methoxyphenyl)-2-propenylidene]amino] phenol (1k)**. Yield; 55%, mp 93–94°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.71 (s, 1H, OH), 8.53 (d, J = 8.9 Hz, 1H, N=CH), 7.66 (d, J = 7.7 Hz, 1H, Ar-H), 7.54 (d, J = 16.1 Hz, 1H, CH), 7.36 (dd, J = 7.7 Hz, 7.9 Hz, 1H, Ar-H), 7.16 (dd, J = 16.1 Hz, 8.9 Hz, 1H, CH), 7.19–6.97 (m, 4H, Ar-H), 6.76 (d, J = 8.3 Hz, 1H, Ar-H), 3.86 (s, 3H, OCH_3), 1.25 (s, 9H, CH_3). *Anal*. Calcd for $C_{20}H_{23}NO_2$: C, 77.63; H, 7.44; N, 4.53. Found: C, 77.62; H, 7.61; N, 4.52.

4-Chloro-2-[[3-(2-methoxyphenyl)-2-propenylidene]amino] phenol (1l). Yield; 45%, mp 79–80°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.26 (s, 1H, OH), 8.45 (d, J = 8.9 Hz, 1H, N=CH), 7.66 (d, J = 7.7 Hz, 1H, Ar-H), 7.55 (d, J = 16.1 Hz, 1H, CH), 7.37 (dd, J = 7.7 Hz, 7.8 Hz, 1H, Ar-H), 7.18–6.97 (m, 5H, Ar-H, CH), 6.84 (d, J = 8.6 Hz, 1H, Ar-H), 3.86 (s, 3H, OCH_3). *Anal*. Calcd for $C_{16}H_{14}ClNO_2$: C, 66.90; H, 4.88; N, 4.88. Found: C, 66.43; H, 4.84; N, 4.74.

General procedure for the synthesis of 2-styrylbenzoxazole by thianthrene cation radical. Modified procedure [9] was adopted as follows. The reaction was carried out with thianthrene cation radical perchlorate (1.0 mmol), **1** (0.5 mmol), and DTBMP (1.50 mmol) in acetonitrile under argon at room temperature. Generally, the colour of the thianthrene cation radical disappeared in 5–10 min. The reaction mixture was neutralized using aqueous sodium bicarbonate solution, followed by extraction of products using dichloromethane.

2-(2-Phenylethenyl)benzoxazole (2a). Colourless crystal with mp 80−81°C (lit. mp 84°C [10]). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.84−7.69 (m, 5H, Ar-H, CH), 7.47−7.29 (m, 6H, Ar-H, CH).

5-Methyl-2-(2-Phenylethenyl)benzoxazole (2b). Colourless crystal with mp 89−91°C (lit. mp 92−93°C [11]). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.79−7.74 (m, 2H, Ar-H), 7.79−7.74 (d, J = 16.4 Hz, 1H, CH), 7.55 (d, J = 8.3 Hz, 1H, Ar-H), 7.51 (s, 1H, Ar-H), 7.45−7.39 (m, 3H, Ar-H), 7.27 (d, J = 16.4 Hz, 1H, CH), 7.18 (d, J = 8.3 Hz, 1H, Ar-H), 2.40 (s, 3H, CH_3).

***5-tert*-Butyl-2-(2-Phenylethenyl)benzoxazole (2c).** Colourless crystal with mp 96−98°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.80−7.74 (m, 2H, Ar-H), 7.80−7.74 (d, J = 16.4 Hz, 1H, CH), 7.68 (s, 1H, Ar-H), 7.58 (d, J = 8.6 Hz, 1H, Ar-H), 7.45−7.39 (m, 4H, Ar-H), 7.30 (d, J = 16.4 Hz, 1H, CH) 1.32 (s, 9H, CH_3).

5-Chloro-2-(2-Phenylethenyl)benzoxazole (2d). Brown crystal with mp 112−113°C (lit. mp 104°C [12]). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.87−7.81 (d, J = 16.6 Hz, 1H, CH), 7.84−7.79 (m, 3H, Ar-H), 7.75 (d, J = 8.7 Hz, 1H, Ar-H), 7.45−7.42 (m, 3H, Ar-H), 7.43 (d, J = 8.7 Hz, 1H, Ar-H), 7.33 (d, J = 16.6 Hz, 1H, CH).

2-[2-(2-Nitrophenyl)ethenyl]benzoxazole (2e). Yellow crystal with mp 138−139°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.12−8.04 (m, 3H, Ar-H), 7.80−7.65 (m, 4H, Ar-H, CH), 7.43−7.36 (m, 3H, Ar-H, CH). *Anal*. Calcd for $C_{15}H_{10}N_2O_3$: C, 67.67; H, 3.76; N, 10.53. Found: C, 66.96; H, 3.72; N, 10.53.

5-Methyl-2-[2-(2-nitrophenyl)ethenyl]benzoxazole (2f). Yellow crystal with mp 131−133°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.12−8.06 (m, 2H, Ar-H), 8.03 (d, J = 16.2 Hz, 1H, CH), 7.82−7.77 (dd, J = 7.7 Hz, 7.5 Hz, 1H, Ar-H), 7.68−7.61 (m, 1H, Ar-H), 7.63−7.61 (d, J = 8.3 Hz, 1H, Ar-H), 7.55 (s, 1H, Ar-H), 7.35 (d, J = 16.2 Hz, 1H, CH), 7.23 (d, J = 8.3 Hz, 1H, Ar-H), 2.41 (s, 3H, CH_3). *Anal*. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.57; H, 4.29; N, 10.00. Found: C, 68.07; H, 4.23; N, 9.99.

***5-tert*-Butyl-2-[2-(2-nitrophenyl)ethenyl]benzoxazole (2g).** Yellow crystal with mp 130−132°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.12 (d, J = 7.9 Hz, 1H, Ar-H), 8.09 (d, J = 7.7 Hz, 1H, Ar-H), 8.05−8.00 (d, J = 16.1 Hz, 1H, N=CH), 7.76 (dd, J = 7.7 Hz, 7.6 Hz, 1H, Ar-H), 7.72 (s, 1H, Ar-H), 7.67−7.61 (d, J = 8.7 Hz, 1H, Ar-H), 7.67−7.61 (dd, J = 7.9 Hz, 7.6 Hz, 1H, Ar-H), 7.50−7.46 (dd, J = 8.7 Hz, 1.94 Hz, 1H, Ar-H), 7.38 (d, 16.1 Hz, 1H, CH), 1.33 (s, 9H, CH_3). *Anal*. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.81; H, 5.59; N, 8.70. Found: C, 70.65; H, 5.68; N, 8.85.

5-Chloro-2-[2-(2-nitrophenyl)ethenyl]benzoxazole (2h). Yellow crystal with mp 153−154°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13−8.07 (m, 2H, Ar-H), 8.13−8.07 (d, J = 16.1 Hz, 1H, CH), 7.89 (s, 1H, Ar-H), 7.83−7.79 (m, 1H, Ar-H), 7.81 (d, J = 8.7 Hz, 1H, Ar-H), 7.67 (t, J = 7.95 Hz, 1H, Ar-H), 7.47 (d, J = 8.7 Hz, 1H, Ar-H), 7.39 (d, 16.1 Hz, 1H, CH). *Anal*. Calcd for $C_{15}H_9ClN_2O_3$: C, 59.90; H, 3.00; N, 9.32. Found: C, 59.36; H, 2.92; N, 9.20.

2-[2-(2-Methoxyphenyl)ethenyl]benzoxazole (2i). Colourless crystal with mp 70−71°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 16.6 Hz, 1H, CH), 7.82 (d, J = 7.7 Hz, 1H, Ar-H), 7.74−7.69 (m, 2H, Ar-H), 7.41−7.32 (m, 3H, Ar-H), 7.29 (d, J = 16.6 Hz, 1H, CH), 7.10 (d, J = 8.1 Hz, 1H, Ar-H), 7.01 (dd, 7.7 Hz, 7.5 Hz, 1H, Ar-H), 3.90(s, 3H, OCH_3). *Anal*. Calcd for $C_{16}H_{13}ClNO_2$: C, 76.49; H, 5.18; N, 5.58. Found: C, 76.35; H, 5.22; N, 5.75.

5-Methyl-2-[2-(2-methoxyphenyl)ethenyl]benzoxazole (2j). Colourless crystal with mp 79−81°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.98 (d, J = 16.5 Hz, 1H, CH), 7.80 (d, J = 7.7 Hz, 1H, Ar-H), 7.57 (d, J = 8.3 Hz, 1H, Ar-H), 7.49 (s, 1H, Ar-H), 7.39 (dd, 8.1 Hz, 7.5 Hz, 1H, Ar-H), 7.25 (d, J = 16.5 Hz, 1H, CH), 7.17 (d, J = 8.3 Hz, 1H, Ar-H), 7.10 (d, J = 8.1 Hz, 1H, Ar-H), 7.00 (dd, J = 7.7 Hz, 7.5 Hz, 1H, Ar-H), 3.90 (s, 3H, OCH_3), 2.40 (s, 3H, CH_3). *Anal*. Calcd for $C_{17}H_{15}NO_2$: C, 76.98; H, 5.66; N, 5.28. Found: C, 76.39; H, 5.66; N, 5.32.

***5-tert*-Butyl-2-[2-(2-methoxyphenyl)ethenyl]benzoxazole (2k).** Crystal with mp 84−85°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.99 (d, J = 16.5 Hz, 1H, CH), 7.82 (d, J = 7.7 Hz, 1H, Ar-H), 7.67 (s, 1H, Ar-H), 7.60 (d, J = 8.6 Hz, 1H, Ar-H), 7.44 (d, J = 8.6 Hz, 1H, Ar-H), 7.40 (dd, J = 7.8 Hz, 7.5 Hz, 1H, Ar-H), 7.28 (d, J = 16.5 Hz, 1H, CH), 7.10 (d, J = 7.8 Hz, 1H, Ar-H), 7.01 (dd, J = 7.7 Hz, 7.5 Hz, 1H, Ar-H), 3.90 (s, 3H, OCH_3), 1.33 (s, 3H, CH_3). *Anal*. Calcd for $C_{20}H_{21}NO_2$: C, 78.18; H, 6.84; N, 4.56. Found: C, 78.10; H, 6.86; N, 4.63.

5-Chloro-2-[2-(2-methoxyphenyl)ethenyl]benzoxazole (2l). Yellow crystal with mp 148−149°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J = 16.6 Hz, 1H, CH), 7.83 (d, J = 7.7 Hz, 1H, Ar-H), 7.80 (s, 1H, Ar-H), 7.75 (d, J = 8.7 Hz, 1H, Ar-H), 7.43−7.40 (d, J = 8.7 Hz, 1H, Ar-H), 7.43−7.40 (m, 1H, Ar-H), 7.29 (d, J = 16.6 Hz, 1H, CH), 7.11 (d, J = 8.40 Hz, 1H, Ar-H), 7.02 (dd, J = 7.7 Hz, 7.3 Hz, 1H, Ar-H), 3.90 (s, 3H, OCH_3). *Anal*. Calcd for $C_{16}H_{12}ClNO_2$: C, 67.37; H, 4.21; N, 4.91. Found: C, 66.41; H, 4.16; N, 4.94.

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