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Synthesis of fluorescent trisubstituted oxazoles via a facile tandem Staudinger/aza-Wittig/isomerization reaction

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ABSTRACT

A new facile synthesis of trisubstituted oxazoles starting from azides was developed. The reactions of azides with triphenyl phosphine afforded the corresponding 2,4,5-trisubstituted oxazole derivatives via tandem Staudinger, aza-Wittig and isomerization reaction either thermally or under basic conditions. Properties of the oxazole derivatives were surveyed and some of the examples showed reasonable fluorescence. The greatest fluorescence intensity was observed when the 2- and the 5- substituents on the oxazole ring were aromatic groups (with $\varepsilon = 2.3–3.0 \times 10^4$ mol^{-1} dm^3 cm^{-1} and $\Phi = 0.25–0.29$ relative to quinine sulphate). However, the fluorescence intensity was diminished when either the 2- or the 5-substituent was H or alkyl.

1. Introduction

Oxazoles, especially fully substituted oxazoles, have been the focus of great interest because of their remarkable biological properties. Some oxazole derivatives were recently found to be good fatty acid amide hydrolase (FAAH) inhibitors [1], complement C3a receptor agonists [2], potent and selective sphingosine-1-phosphate agonists [3], anti-HIV agents [4], anti-tuberculotic agents [5] and antifungal agents [6]. The oxazole nucleus is also ubiquitous in natural products such as pyrronazol [7], ulapualides [8], diazonamides [9], and rhizopodin [10]. In addition, oxazole derivatives have exhibited a high potential as efficient luminophores for liquid and fluorescent probes and markers in biological or supramolecular systems [11]. Owing to the structural diversity and complexity of these oxazoles, many new method have been developed for their synthesis to deduce structure-activity relationships and discover new analogues with improved properties [12–19]. For example, Jiang et al. recently reported a palladium-catalyzed sequential reaction to prepare oxazole derivatives from amides and ketones [12]. *N*-Iodosuccinimide (NIS) mediated cyclization of propargylamides was also used to synthesize the oxazole derivatives in good yields [13]. Tojo et al. reported a one-pot preparation of 2,5-disubstituted and 2,4,5-trisubstituted oxazoles by the reaction of aromatic ketones with nitriles in the presence of molecular iodine and oxone [14]. Meanwhile, our group developed reaction sequences to prepare oxazoles from iminophosphoranes [20]. In spite of the above advances, there is still a need for a convenient synthesis of 2,4,5-trisubstituted oxazoles from readily available starting materials.

The aza-Wittig reactions have received attention in synthetic organic chemistry because of their ability to create structurally diverse heterocyclic compounds from simple precursors in an efficient manner [21]. Continuing our interest in the synthesis of *N*-heterocycles via the aza-Wittig reaction [22], we wish to report herein a facile synthesis of 2,4,5-trisubstituted oxazoles by a tandem Staudinger/aza-Wittig/isomerization reaction starting from easily accessible vinyl azides **3**. We also surveyed their fluorescence properties in order to test their possible use as fluorescent probes.

2. Results and discussion

Vinyl azide **1** was obtained easily either from the condensation of the α-azidoketone with aromatic aldehydes in the presence of piperidinium acetate, or from the reaction of dibromides with sodium azide according to literature reports [23,24]. Reduction of the vinyl azides **1** with $NaBH_4$ in methanol at 0 °C gave the azides 2 in good yields (81–92%, Scheme 1, Table 1). The reaction of azides **2** with various acyl chlorides in the presence of NEt_3 produced the azides **3** in 70–90% yields (Scheme 1, Table 2).

When azides **3** were treated with triphenylphosphine in dry

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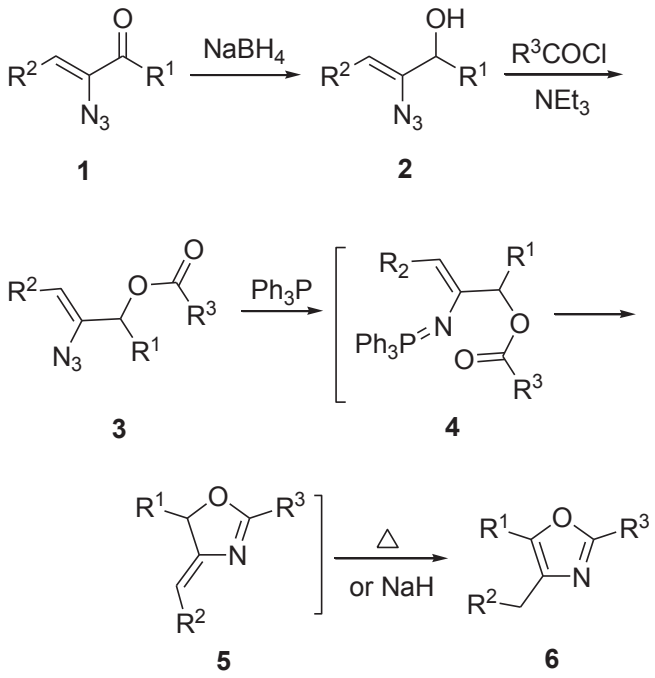

Scheme 1. Preparation of vinyl azides **2**, **3** and oxazoles **6.**

Table 1
Preparation of vinyl azides **2**.

	R^1	R^2	Yield[a](%)
2a	H	Ph	92
2b	Ph	Ph	84
2c	Ph	4-ClC_6H_4	87
2d	4-ClC_6H_4	Ph	90
2e		Ph	81
2f	CH_3	Ph	89

[a] Isolated yields based on azides **1**.

toluene at room temperature, and then at reflux for 4–10 h, the oxazole derivatives **6c**-**6o** were isolated directly in good yields in most cases (61–85%, Scheme 1, Table 2, entry 2–15). Though a mixture of **5** and **6** often resulted, in other cases (Scheme 1, Table 2, entry 1–2 and entry 16–19), compounds **6a**-**6b** and **6p**-**6s** could be obtained in 71–84% overall yields by further treating the reaction mixture with sodium hydride at room temperature. The tandem formation of oxazoles **6** can be viewed as an initial Staudinger reaction between the azide **5** and triphenylphosphine to create the iminophosphorane intermediate **4**. Further intramolecular aza-Wittig reaction of **4** produces dihydrooxazoles **5**, in which an isomerization reaction takes place to give the aromatized oxazoles **6** under either heating or basic conditions. It's noteworthy that the reaction proceeds under mild conditions to give various 2,4,5-trisubstituted oxazoles **6**, and the overall transformation is run in a simple one-pot procedure from azides **3** in good overall yields.

The structure of the 2,4,5-trisubstituted oxazoles **6** was confirmed from their spectroscopic data. For example, the ^{1}H NMR spectral data of **6a** shows a singlet at 3.93 ppm due to the hydrogen of CH_2. The signals attributable to the protons of the aromatic ring are found at 7.94–7.24 ppm as multiplets. The ^{13}C NMR spectrum data in **6a** show the signals of the C-2 carbon of the oxazole at 160.7 ppm. The signals of CH_2 are found at 33.0 ppm. The mass spectrum of **6a** shows a molecular ion peak at *m*/*z* 269 with 95% abundance.

The fluorescence properties of compounds **6a**, **6d**, **6h**, **6l**, **6n**, and **6p** were studied in ethanol. These compounds present comparable molar absorption coefficients with literature reported oxazoles [11c,e]. The fluorescence spectra of these compounds are presented in Fig. 1. The fluorescence intensity of the compounds **6d**, **6h**, **6l** and **6n** is far stronger than that of the compounds **6a** and **6p**. This implies that stronger fluorescence intensity is resulted as both of R^1 and R^3 on oxazole ring are aromatic substituents (compounds **6d**, **6h**, **6l** and **6n**) which present a more extended aromatic system. However, the fluorescence intensity is reduced when R^1 or R^3 is a hydrogen or alkyl substituent (compounds **6a** and **6p**). The maximum absorption (λ_{abs}) and emission (λ_{em}) wavelengths, molar absorption coefficients (ε), and quantum yield (Φ_s) of the oxazole derivatives are presented in Table 3.

3. Conclusion

In summary, we have developed an efficient synthetic procedure to access 2,4,5-trisubstituted oxazoles. Our method has a significant implication for the synthesis of a variety of fully substituted oxazole derivatives. In addition, these reactions have the advantages of mild reaction conditions, easily accessible starting materials and good yields. Furthermore, the photophysical properties carried out with some of the oxazole derivatives indicate that they may be useful in future fluorescent probes.

4. Experimental

Column chromatography purifications were performed under "flash" conditions using 400–630 mesh silica gel, except where otherwise noted. Analytical thin-layer chromatography (TLC) was carried out on silica gel 60 F254 plates, which were visualized by exposure to ultraviolet light.

Instrumentation: Melting points were determined using a X-4 model apparatus and were uncorrected. IR spectra were recorded on a PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. MS were measured on a Finnigan Trace MS spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury Plus 600 (600 MHz) spectrometer and chemical shifts (δ) were given in ppm using $(CH_3)_4Si$ as an internal reference ($\delta = 0$). Elemental analyses were taken on a Vario EL III elementary analysis instrument.

4.1. Synthetic details

4.1.1. Preparation of azides *2*

A methanol (20 mL) solution of vinyl azides **1** (8 mmol) was cooled to 0 °C and $NaBH_4$ (0.15 g, 4 mmol) was added. Vigorous gas evolution occurred. After stirred for 10 min at 0 °C, the reaction mixture was poured into 1 N HCl (30 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. The solution was concentrated in vacuo and the residue was purified by chromatography eluting with EtOAc/petroleum ether (1:1) to give compounds **2**.

*4.1.1.1. 2-Azido-3-phenylprop-2-en-1-ol (**2a**).* light yellow solid (1.29 g, 92%). mp. 39–41 °C. IR (KBr): 3386, 2106, 1644, 1491, 1261 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta = 7.62$ (d, $J = 5.4$ Hz, 2H, Ar-H), 7.33–7.23 (m, 3H, Ar-H), 5.81 (s, 1H, =CH), 4.47 (s, 2H, CH_2), 1.91 (br, 1H, OH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 134.3, 134.1, 128.8, 128.1, 127.3, 116.3, 64.6. Elemental Anal. Calcd for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.93; H, 5.38; N, 23.81.

Table 2
Preparation of vinyl azides **3** and oxazoles **6**.

Entry	R^1	R^2	R^3	Compd	Yield[a] (%)	Compd	Yield[b] (%)
1	H	Ph	4-ClC_6H_4	**3a**	85	**6a**	74
2	H	Ph	4-$NO_2C_6H_4$	**3b**	90	**6b**	82
3	Ph	Ph	Ph	**3c**	87	**6c**	69
4	Ph	Ph	4-ClC_6H_4	**3d**	83	**6d**	78
5	Ph	Ph	4-$NO_2C_6H_4$	**3e**	82	**6e**	69
6	Ph	Ph	4-$CH_3C_6H_4$	**3f**	80	**6f**	71
7	Ph	Ph	2-ClC_6H_4	**3g**	86	**6g**	85
8	Ph	4-ClC_6H_4	4-ClC_6H_4	**3h**	88	**6h**	78
9	Ph	4-ClC_6H_4	2-ClC_6H_4	**3i**	90	**6i**	72
10	Ph	4-ClC_6H_4	4-$NO_2C_6H_4$	**3j**	89	**6j**	68
11	4-ClC_6H_4	Ph	4-$NO_2C_6H_4$	**3k**	85	**6k**	83
12	4-ClC_6H_4	Ph	4-ClC_6H_4	**3l**	89	**6l**	76
13	4-ClC_6H_4	Ph	2-ClC_6H_4	**3m**	81	**6m**	72
14		Ph	4-ClC_6H_4	**3n**	70	**6n**	69
15		Ph	4-$NO_2C_6H_4$	**3o**	73	**6o**	61
16	Ph	Ph	CH_3	**3p**	72	**6p**	74
17	4-ClC_6H_4	Ph	CH_3	**3q**	76	**6q**	71
18	Ph	Ph	*n*-Pr	**3r**	79	**6r**	79
19	CH_3	Ph	Ph	**3s**	87	**6s**	84

[a] Isolated yields based on azides **2**.
[b] Isolated yields based on azides **3**.

*4.1.1.2. 2-Azido-1,3-diphenylprop-2-en-1-ol (**2b**).* yellow oil (1.69 g, 84%). IR (KBr): 3373, 2107, 1638, 1492, 1259 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.62 (d, J = 7.2 Hz, 2H, Ar-H), 7.48 (d, J = 7.2 Hz, 2H, Ar-H), 7.38–7.19 (m, 6H, Ar-H), 5.87 (s, 1H, =CH), 5.48 (s, 1H, OCH), 2.76 (br, 1H, OH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 139.2, 136.0, 134.3, 129.0, 128.9, 128.8, 128.6, 128.3, 128.1, 127.4, 126.3, 116.3, 76.3. Elemental Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.75; H, 5.45; N, 16.81.

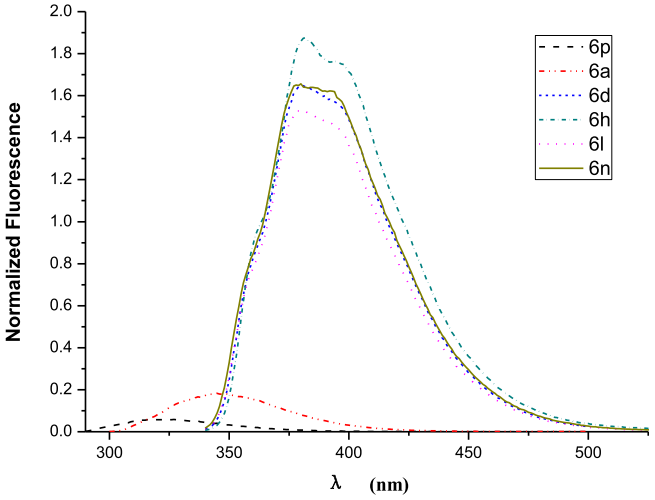

Fig. 1. Fluorescence spectra at 25 °C of solution (2×10^{-5} mol dm^{-3}) of compound **6a, 6p 6d, 6h, 6l,** and **6n** in ethanol.

Table 3
Luminescent properties of **6** in ethanol.

Entry	Comp	ε (10^4 mol^{-1} dm^3 cm^{-1})	λ_{abs} (nm)	λ_{em} (nm)	Φ^c
1	**6a**[a]	2.3	292	344	0.28
2	**6d**[b]	2.3	327	380	0.27
3	**6h**[b]	3.0	330	380	0.29
4	**6l**[b]	2.4	325	377	0.25
5	**6n**[b]	2.9	325	383	0.26
6	**6p**[a]	2.1	277	325	0.10

[a] Excitation at 276 nm, relative to phenol (Φ = 0.14 at 25 °C) for **6a**, **6p**.
[b] Excitation at 351 nm, relative to quinine sulphate (0.1 M L^{-1}, Φ = 0.577 at 25 °C) for **6d**, **6h**, **6l**, **6n**.
[c] Error about ±10%.

*4.1.1.3. 2-Azido-3-(4-chlorophenyl)-1-phenylprop-2-en-1-ol (**2c**).* light yellow oil (1.98 g, 87%). IR (KBr): 3359, 2109, 1638, 1490, 1282 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.63 (d, J = 7.8 Hz, 2H, Ar-H), 7.47 (d, J = 7.8 Hz, 2H, Ar-H), 7.38–7.23 (m, 5H, Ar-H), 5.90 (s, 1H, =CH), 5.54 (s, 1H, OCH), 2.56 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 139.1, 136.6, 132.8, 130.2, 128.8, 128.5, 128.3, 126.4, 114.9, 76.1. Elemental Anal. Calcd for $C_{15}H_{12}ClN_3O$: C, 63.05; H, 4.23; N, 14.71. Found: C, 63.27; H, 4.34; N, 14.64.

*4.1.1.4. 2-Azido-1-(4-chlorophenyl)-3-phenylprop-2-en-1-ol (**2d**).* light yellow solid (2.05 g, 90%). mp. 97–99 °C. IR (KBr): 3451, 2103, 1630, 1490, 1281 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.60 (d, J = 7.8 Hz, 2H, Ar-H), 7.39 (d, J = 8.4 Hz, 2H, Ar-H), 7.32–7.20 (m, 5H, Ar-H), 5.81 (s, 1H, =CH), 5.42 (s, 1H, OCH), 2.88 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 137.5, 135.5, 134.0, 129.0, 128.9, 128.7, 128.3, 128.1, 127.9, 127.7, 127.4, 116.7, 75.9. Elemental Anal. Calcd for $C_{15}H_{12}ClN_3O$: C, 63.05; H, 4.23; N, 14.71. Found: C, 62.84; H, 4.41; N, 14.78.

*4.1.1.5. 2-Azido-3-(furan-2-yl)-1-phenylprop-2-en-1-ol (**2e**).* light yellow oil (1.56 g, 81%). IR (KBr): 3370, 2105, 1643, 1483, 1261 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.49 (d, J = 7.2 Hz, 2H, Ar-H), 7.42–7.35 (m, 4H, Ar-H), 6.77–6.44 (m, 2H, Ar-H), 5.87 (s, 1H, =CH), 5.56 (s, 1H, OCH), 2.48 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 150.0,141.5, 141.2, 139.0, 134.5, 128.8, 128.6, 126.6, 126.4, 111.8, 110.1, 105.6, 75.2. Elemental Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.57; H, 4.85; N, 17.53.

*4.1.1.6. 3-Azido-4-phenylbut-3-en-2-ol (**2f**).* yellow oil (1.35 g, 89%). IR (KBr): 3379, 2110, 1641, 1491, 1320, 1066 cm^{-1}. ^1H NMR ($CDCl_3$,

600 MHz): $\delta = 7.62$ (d, $J = 7.2$ Hz, 2H, Ar-H), 7.34–7.21 (m, 3H, Ar-H), 5.82 (s, 1H, =CH), 4.68–4.64 (m, 1H, OCH), 1.94 (s, 1H, OH), 1.57 (d, $J = 6.0$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 137.8, 134.4, 129.0, 128.8, 128.3, 128.2, 127.3, 127.2, 114.0, 70.3, 22.3. Elemental Anal. Calcd for $C_{10}H_{11}N_3O$: C, 63.48; H, 5.86; N, 22.21. Found: C, 63.59; H, 5.68; N, 22.34.

4.1.2. Preparation of azides ***3***

A solution of azido alcohol **2** (5 mmol) in dry methylene chloride (20 mL) was added dropwise under nitrogen to a solution of acyl chloride (5 mmol) and triethylamine (10 mmol) in dry methylene chloride (10 mL) at 0 °C. After the stirring was continued for 0.5 h, the reaction mixture was slowly warmed to room temperature while the stirring was continued until the reaction completed based on TLC monitoring. The solution was concentrated in vacuo and the residue was purified by chromatography eluting with EtOAc/petroleum ether (1:3) to give compounds **3**.

*4.1.2.1. 2-Azido-3-phenylallyl 4-chlorobenzoate (**3a**).* white solid (1.33 g, 85%). mp. 102–103 °C. IR (KBr): 2111, 1722, 1645, 1289, 1119 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta = 8.02$ (d, $J = 8.4$ Hz, 2H, Ar-H), 7.66 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.45–7.26 (m, 5H, Ar-H), 6.00 (s, 1H, =CH), 5.14 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 164.5, 134.0, 132.9, 131.6, 131.3, 131.1, 129.2, 128.3, 128.1, 126.7, 120.4, 66.2. Elemental Anal. Calcd for $C_{16}H_{12}ClN_3O_2$: C, 61.25; H, 3.86; N, 13.39. Found: C, 61.41; H, 4.06; N, 13.32.

*4.1.2.2. 2-Azido-3-phenylallyl 4-nitrobenzoate (**3b**).* yellow solid (1.46 g, 90%). mp. 105–107 °C. IR (KBr): 2110, 1722, 1645, 1271, 1073 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta = 8.33$ (d, $J = 8.4$ Hz, 2H, Ar-H), 8.27 (d, $J = 9.0$ Hz, 2H, Ar-H), 7.67 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.37–7.26 (m, 3H, Ar-H), 6.04 (s, 1H, =CH), 5.21 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 163.9, 150.7, 134.7, 133.6, 131.0, 130.8, 129.3, 129.1, 128.2, 123.6, 120.9, 66.9. Elemental Anal. Calcd for $C_{16}H_{12}N_4O_4$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.39; H, 3.92; N, 17.55.

*4.1.2.3. 2-Azido-1,3-diphenylallyl benzoate (**3c**).* yellow solid (1.54 g, 87%). mp. 95–96 °C. IR (KBr): 2100, 1734, 1634, 1448, 1262 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta =$ 8.21–7.24 (m, 15H, Ar-H), 6.94 (s, 1H, =CH), 6.08 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 165.0, 136.2, 133.9, 133.5, 132.3, 130.0, 129.8, 129.3, 129.2, 129.1, 128.9, 128.7, 128.5, 128.3, 128.1, 127.9, 127.6, 126.4, 119.5, 119.3, 76.8. Elemental Anal. Calcd for $C_{22}H_{17}N_3O_2$: C, 74.35; H, 4.82; N, 11.82. Found: C, 74.12; H, 4.66; N, 11.97.

*4.1.2.4. 2-Azido-1,3-diphenylallyl 4-chlorobenzoate (**3d**).* light yellow solid (1.61 g, 83%). mp. 96–97 °C. IR (KBr): 2108, 1728, 1632, 1448, 1264, 1100 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta =$ 8.12 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.67 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.53–7.25 (m, 10H, Ar-H), 6.91 (s, 1H, =CH), 6.06 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 164.2, 140.1, 136.0, 133.8, 132.0, 131.3, 131.2, 129.3, 129.2, 129.1, 128.9, 128.8, 128.3, 128.1, 127.9, 127.8, 126.4, 126.2, 119.7, 119.5, 77.8. Elemental Anal. Calcd for $C_{22}H_{16}ClN_3O_2$: C, 67.78; H, 4.14; N, 10.78. Found: C, 68.03; H, 4.30; N, 10.74.

*4.1.2.5. 2-Azido-1,3-diphenylallyl 4-nitrobenzoate (**3e**).* yellow solid (1.64 g, 82%). mp. 52–54 °C. IR (KBr): 2106, 1732, 1640, 1494, 1261, 1097 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta = 8.36$ (s, 4H, Ar-H), 7.67 (d, $J = 7.2$ Hz, 2H, Ar-H), 7.54–7.26 (m, 8H, Ar-H), 6.94 (s, 1H, =CH), 6.08 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 163.2, 150.8, 135.5, 134.7, 133.6, 131.6, 131.1, 129.3, 129.2, 129.1, 128.9, 128.4, 128.2, 126.4, 126.3, 123.9, 123.6, 120.1, 119.9, 78.6. Elemental Anal. Calcd for $C_{22}H_{16}N_4O_4$: C, 66.00; H, 4.03; N, 13.99. Found: C, 66.21; H, 4.16; N, 14.22.

*4.1.2.6. 2-Azido-1,3-diphenylallyl 4-methylbenzoate (**3f**).* light yellow solid (1.47 g, 80%). mp. 45–47 °C. IR (KBr): 2105, 1726, 1612, 1493, 1262, 1089 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta =$ 8.08 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.67 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.54 (d, $J = 7.2$ Hz, 2H, Ar-H), 7.44–7.23 (m, 8H, Ar-H), 6.92 (s, 1H, =CH), 6.06 (s, 1H, CH), 2.44 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 165.1, 144.4, 136.3, 134.0, 132.4, 130.0, 129.9, 129.5, 129.4, 129.3, 129.2, 129.0, 128.9, 128.7, 128.3, 128.1, 126.6, 126.5, 126.3, 119.4, 119.2, 60.7, 21.8. Elemental Anal. Calcd for $C_{23}H_{19}N_3O_2$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.70; H, 4.95; N, 11.57.

*4.1.2.7. 2-Azido-1,3-diphenylallyl 2-chlorobenzoate (**3g**).* light yellow solid (1.67 g, 86%). mp. 80–82 °C. IR (KBr): 2118, 1733, 1642, 1450, 1247, 1110 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta =$ 8.02 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.66 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.56–7.25 (m, 11H, Ar-H), 6.91 (s, 1H, =CH), 6.09 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 163.8, 135.8, 134.2, 133.8, 131.9, 131.7, 131.4, 131.2, 129.2, 129.1, 128.8, 128.7, 128.6, 128.3, 128.1, 126.8, 126.6, 126.5, 119.5, 77.7. Elemental Anal. Calcd for $C_{22}H_{16}ClN_3O_2$: C, 67.78; H, 4.14; N, 10.78. Found: C, 68.06; H, 4.20; N, 10.95.

*4.1.2.8. 2-Azido-1-(4-chlorophenyl)-3-phenylallyl 4-chlorobenzoate (**3h**).* light yellow solid (1.86 g, 88%). mp. 87–89 °C. IR (KBr): 2107, 1732, 1641, 1492, 1262, 1092 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta =$ 8.10 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.66 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.50–7.26 (m, 9H, Ar-H), 6.86 (s, 1H, =CH), 6.05 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 164.1, 140.3, 134.8, 134.6, 133.6, 131.7, 131.2, 129.3, 129.2, 129.0, 128.4, 128.2, 127.9, 127.7, 119.8, 76.8. Elemental Anal. Calcd for $C_{22}H_{15}Cl_2N_3O_2$: C, 62.28; H, 3.56; N, 9.90. Found: C, 62.46; H, 3.78; N, 9.95.

*4.1.2.9. 2-Azido-1-(4-chlorophenyl)-3-phenylallyl 2-chlorobenzoate (**3i**).* light yellow solid (1.90 g, 90%). mp. 48–50 °C. IR (KBr): 2111, 1723, 1643, 1489, 1272, 1094 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta =$ 8.01 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.66 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.53–7.25 (m, 10H, Ar-H), 6.86 (s, 1H, =CH), 6.09 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 163.9, 134.8, 134.5, 134.4, 133.7, 133.4, 131.8, 131.6, 129.3, 129.2, 129.0, 128.7, 128.4, 128.3, 128.2, 128.1, 126.9, 126.7, 119.9, 119.7, 77.3. Elemental Anal. Calcd for $C_{22}H_{15}Cl_2N_3O_2$: C, 62.28; H, 3.56; N, 9.90. Found: C, 62.57; H, 3.43; N, 10.11.

*4.1.2.10. 2-Azido-1-(4-chlorophenyl)-3-phenylallyl 4-nitrobenzoate (**3j**).* yellow solid (1.93 g, 89%). mp. 58–60 °C. IR (KBr): 2108, 1738, 1641, 1492, 1291, 1110 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta = 8.36$ (d, $J = 9.0$ Hz, 2H, Ar-H), 8.33 (d, $J = 9.0$ Hz, 2H, Ar-H), 7.66 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.48–7.26 (m, 7H, Ar-H), 6.90 (s, 1H, =CH), 6.08 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 163.2, 150.9, 135.0, 134.4, 134.1, 133.4, 131.2, 131.1, 130.9, 130.7, 129.3, 129.2, 129.1, 128.4, 128.2, 127.9, 127.7, 123.9, 120.4, 78.0. Elemental Anal. Calcd for $C_{22}H_{15}ClN_4O_4$: C, 60.77; H, 3.48; N, 12.88. Found: C, 60.94; H, 3.62; N, 13.14.

*4.1.2.11. 2-Azido-3-(4-chlorophenyl)-1-phenylallyl 4-nitrobenzoate (**3k**).* yellow solid (1.84 g, 85%). mp. 116–118 °C. IR (KBr): 2099, 1735, 1640, 1491, 1260, 1093 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta = 8.35$ (s, 4H, Ar-H), 7.61 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.53–7.29 (m, 7H, Ar-H), 6.93 (s, 1H, =CH), 6.00 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ 163.1, 150.7, 135.3, 134.4, 133.4, 132.2, 132.1, 130.9, 130.4, 129.0, 128.3, 126.3, 123.7, 118.5, 118.4, 78.3. Elemental Anal. Calcd for $C_{22}H_{15}ClN_4O_4$: C, 60.77; H, 3.48; N, 12.88. Found: C, 60.81; H, 3.25; N, 12.82.

*4.1.2.12. 2-Azido-3-(4-chlorophenyl)-1-phenylallyl-4-chlorobenzoate (**3l**).* light yellow solid (1.88 g, 89%). mp. 98–100 °C. IR (KBr): 2102,

1726, 1637, 1489, 1260, 1094 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 8.11 (d, J = 8.4 Hz, 2H, Ar-H), 7.60 (d, J = 8.4 Hz, 2H, Ar-H), 7.51–7.25 (m, 9H, Ar-H), 6.89 (s, 1H, =CH), 5.98 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 164.2, 140.2, 135.8, 133.4, 132.7, 132.3, 131.2, 130.5, 129.0, 128.9, 128.4, 127.7, 126.3, 118.2, 118.1, 77.7. Elemental Anal. Calcd for $C_{22}H_{15}Cl_2N_3O_2$: C, 62.28; H, 3.56; N, 9.90. Found: C, 62.45; H, 3.70; N, 10.14.

*4.1.2.13. 2-Azido-3-(4-chlorophenyl)-1-phenylallyl-2-chlorobenzoate (**3m**).* light yellow solid (1.71 g, 81%). mp. 87–89 °C. IR (KBr): 2101, 1745, 1638, 1490, 1282, 1096 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 8.01 (d, J = 7.2 Hz, 1H, Ar-H), 7.61–7.25 (m, 12H, Ar-H), 6.90 (s, 1H, =CH), 6.02 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 163.8, 135.6, 134.3, 133.2, 132.6, 132.4, 131.7, 131.4, 130.5, 128.9, 128.7, 128.3, 126.8, 126.6, 118.0, 117.9, 77.6. Elemental Anal. Calcd for $C_{22}H_{15}Cl_2N_3O_2$: C, 62.28; H, 3.56; N, 9.90. Found: C, 62.53; H, 3.79; N, 9.73.

*4.1.2.14. 2-Azido-3-(furan-2-yl)-1-phenylallyl 4-chlorobenzoate (**3n**).* light yellow solid (1.33 g, 70%). mp. 66–68 °C. IR (KBr): 2108, 1741, 1643, 1492, 1261, 1089 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 8.36–8.32 (m, 4H, Ar-H), 7.51–7.39 (m, 6H, Ar-H), 6.89 (s, 1H, =CH), 6.83–6.46 (m, 2H, Ar-H), 6.00 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 164.2, 149.5, 141.8, 135.8, 132.6, 131.3, 130.9, 130.5, 129.1, 128.9, 127.7, 126.5, 111.1, 110.9, 108.6, 108.4, 61.2. Elemental Anal. Calcd for $C_{20}H_{14}ClN_3O_3$: C, 63.25; H, 3.72; N, 11.06. Found: C, 63.54; H, 3.91; N, 11.17.

*4.1.2.15. 2-Azido-3-(furan-2-yl)-1-phenylallyl 4-nitrobenzoate (**3o**).* yellow solid (1.42 g, 73%). mp. 80–82 °C. IR (KBr): 2110, 1739, 1637, 1492, 1282, 1110 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 8.01 (d, J = 8.4 Hz, 2H, Ar-H), 7.50–7.37 (m, 8H, Ar-H), 6.86 (s, 1H, =CH), 6.86 (s, 1H, =CH), 6.81–6.45 (m, 2H, ArH), 5.98 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 163.2, 150.8, 149.4, 141.9, 135.3, 134.6, 131.1, 130.0, 129.1, 126.5, 123.9, 123.3, 112.0, 111.4, 108.8, 61.9. Elemental Anal. Calcd for $C_{20}H_{14}N_4O_5$: C, 61.54; H, 3.62; N, 14.35. Found: C, 61.59; H, 3.79; N, 14.59.

*4.1.2.16. 2-Azido-1,3-diphenylallyl acetate (**3p**).* light yellow oil (1.05 g, 72%). mp. 60–63 °C. IR (KBr): 2107, 1752, 1641, 1494, 1293, 1222, 1023 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.63 (d, J = 7.2 Hz, 2H, Ar-H), 7.46–7.24 (m, 8H, Ar-H), 6.64 (s, 1H, =CH), 5.93 (s, 1H, CH), 2.25 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 169.4, 136.2, 133.9, 132.4, 129.2, 129.1, 128.9, 128.8, 128.7, 128.3, 128.1, 126.7, 126.5, 119.0, 118.8, 76.5, 21.0. Elemental Anal. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.69; H, 5.37; N, 14.54.

*4.1.2.17. 2-Azido-3-(4-chlorophenyl)-1-phenylallyl acetate (**3q**).* light yellow oil (1.24 g, 76%). mp. 88–90 °C. IR (KBr): 2109, 1756, 1641, 1490, 1291, 1222,1087 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.57 (d, J = 8.4 Hz, 2H, Ar-H), 7.45–7.25 (m, 7H, Ar-H), 6.62 (s, 1H, =CH), 5.85 (s, 1H, CH), 2.25 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 169.3, 135.9, 133.1, 133.0, 132.4, 130.4, 128.8, 128.3, 126.5, 117.4, 117.3, 76.5, 21.0. Elemental Anal. Calcd for $C_{17}H_{14}ClN_3O_2$: C, 62.30; H, 4.31; N, 12.82. Found: C, 62.17; H, 4.37; N, 12.65.

*4.1.2.18. 2-Azido-1,3-diphenylallyl butyrate (**3r**).* light yellow oil (1.27 g, 79%). IR (KBr): 2108, 1745, 1641, 1494, 1294, 1161, 1079 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.63 (d, J = 8.4 Hz, 2H, Ar-H), 7.46–7.24 (m, 8H, Ar-H), 6.66 (s, 1H, =CH), 5.93 (s, 1H, CH), 2.49 (t, J = 7.2 Hz, 2H, CH_2), 1.78–1.74 (m, 2H, CH_2), 1.00 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 172.0, 136.4, 134.0, 132.6, 129.2, 129.1, 128.6, 128.3, 128.1, 127.8, 126.7, 126.5, 119.0, 76.3, 36.3, 18.3, 13.5. Elemental Anal. Calcd for $C_{19}H_{19}N_3O_2$: C, 71.01; H, 5.96; N, 13.08. Found: C, 71.23; H, 6.13; N, 13.36.

*4.1.2.19. 3-Azido-4-phenylbut-3-en-2-yl benzoate (**3s**).* light yellow oil (1.27 g, 87%). IR (KBr): 2107, 1722, 1642, 1450, 1266, 1095 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 8.10 (d, J = 7.2 Hz, 2H, Ar-H), 7.65–7.23 (m, 8H, Ar-H), 5.98 (s, 1H, =CH), 5.92 (q, J = 7.2 Hz, 1H, CH), 1.73 (d, J = 6.6 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 165.2, 134.0, 133.9, 133.3, 129.9, 129.6, 129.1, 128.5, 128.4, 128.3, 128.1, 127.6, 117.3, 73.1, 19.3. Elemental Anal. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.74; H, 5.32; N, 14.49.

*4.1.3. Preparation of oxazoles **6***

To a solution of triphenyl phosphine (0.52 g, 2 mmol) in dry toluene (10 mL) was added dropwise azide **3** (2 mmol) at room temperature. The reaction mixture was stirred for further 2 h, and then heated at refluxing temperature for 4–10 h (6 h for compounds **6d**-**6j**; 4 h for compounds **6k**-**6m**; 10 h for **6n**-**6o**). For the preparation of compounds **6a**-**6b** and **6p**-**6s**, NaH (0.005 g, 0.2 mmol) was added and the reaction mixture was stirred for 1–2 h at room temperature. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column, eluting with petroleum ether (60–90 °C)/ethyl acetate (7:1), to afford **6**.

*4.1.3.1. 4-Benzyl-2-(4-chlorophenyl)oxazole (**6a**).* light yellow solid (0.40 g, 74%). mp. 69–70 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.94 (d, J = 8.4 Hz, 2H, Ar-H), 7.40 (d, J = 8.4 Hz, 2H, Ar-H), 7.34–7.24 (m, 6H, Ar-H), 3.93 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 160.7, 142.1, 138.1, 136.2, 135.3, 135.0, 129.1, 129.0, 128.8, 128.7, 128.4, 127.6, 127.5, 33.0. MS: m/z (%) = 269 (95, M^+), 240(8), 139 (100), 103 (31), 91 (29), 77 (19). Elemental Anal. Calcd for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.48; N, 5.19. Found: C, 71.49; H, 4.36; N, 5.40.

*4.1.3.2. 4-Benzyl-2-(4-nitrophenyl)oxazole (**6b**).* yellow solid (0.46 g, 82%). mp. 104–106 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ = 8.29 (d, J = 8.4 Hz, 2H, Ar-H), 8.18 (d, J = 8.4 Hz, 2H, Ar-H), 7.41–7.23 (m, 6H, Ar-H, =CH), 3.97 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 159.4, 148.3, 142.9, 137.8, 136.3, 132.7, 128.7, 128.5, 126.8, 126.6, 123.9, 32.8. MS: m/z (%) = 280 (100, M^+), 150 (53), 131 (23), 103 (22), 91 (25), 77 (15). Elemental Anal. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.56; H, 4.32; N, 9.99. Found: C, 68.61; H, 4.56; N, 9.85.

*4.1.3.3. 4-Benzyl-2,5-diphenyloxazole (**6c**).* light yellow solid (0.43 g, 69%). mp. 94–95 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ = 8.11–7.22 (m, 15H, Ar-H), 4.22 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 159.8, 146.4, 138.5, 135.6, 132.0, 131.9, 130.2, 128.8, 128.6, 128.5, 128.3, 127.9, 127.4, 126.3, 125.5, 33.0. MS: m/z (%) = 311 (100, M^+), 207 (31), 165 (20), 105 (49), 77 (59). Elemental Anal. Calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 85.01; H, 4.76; N, 4.55.

*4.1.3.4. 4-Benzyl-2-(4-chlorophenyl)-5-phenyloxazole (**6d**).* white solid (0.54 g, 78%). mp. 133–134 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ = 8.04 (d, J = 7.2 Hz, 2H, Ar-H), 7.66 (d, J = 6.6 Hz, 2H, Ar-H), 7.45–7.23 (m, 10H, Ar-H), 4.21 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 158.9, 146.8, 138.4, 136.3, 135.8, 131.8, 129.3, 129.0, 128.9, 128.6, 128.5, 128.4, 128.2, 127.6, 126.4, 125.9, 125.6, 33.0. MS: m/z (%) = 345 (100, M^+), 207 (39), 179 (11), 139 (46), 77 (76). Elemental Anal. Calcd for $C_{22}H_{16}ClNO$: C, 76.41; H, 4.66; N, 4.05. Found: C, 76.22; H, 4.84; N, 4.14.

*4.1.3.5. 4-Benzyl-2-(4-nitrophenyl)-5-phenyloxazole (**6e**).* yellow solid (0.49 g, 69%). mp. 174–176 °C. ^1H NMR ($CDCl_3$, 600 MHz): δ = 8.32–8.26 (m, 4H, Ar-H), 7.68–7.25 (m, 10H, Ar-H), 4.23 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 157.5, 148.3, 148.0,

138.1, 136.8, 132.7, 128.9, 128.6, 128.3, 127.9, 126.8, 126.5, 125.8, 124.1, 33.0. MS: *m/z* (%) = 356 (20, M^+), 249 (20), 207 (56), 179 (43), 105 (65), 77 (100). Elemental Anal. Calcd for $C_{22}H_{16}N_2O_3$: C, 74.15; H, 4.53; N, 7.86. Found: C, 74.31; H, 4.65; N, 8.05.

*4.1.3.6. 4-Benzyl-5-phenyl-2-p-tolyloxazole (**6f**).* white solid (0.46 g, 71%). mp. 108–109 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.00 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.66 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.43–7.23 (m, 10H, Ar-H), 4.21 (s, 2H, CH_2), 2.41 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 160.1, 146.1, 140.5, 138.6, 135.5, 129.4, 128.8, 128.5, 128.4, 127.8, 126.3, 125.5, 124.7, 33.1, 21.5. MS: *m/z* (%) = 325 (100, M^+), 207 (25), 165 (16), 119 (28), 105 (19), 77 (43). Elemental Anal. Calcd for $C_{23}H_{19}NO$: calcd. C, 84.89; H, 5.89; N, 4.30. Found: C, 84.72; H, 6.09; N, 4.28.

*4.1.3.7. 4-Benzyl-2-(2-chlorophenyl)-5-phenyloxazole (**6g**).* white solid (0.59 g, 85%). mp. 85–86 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.10 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.69 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.52–7.22 (m, 11H, Ar-H), 4.25 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 157.9, 147.1, 138.5, 135.5, 132.3, 131.2, 131.0, 130.9, 128.8, 128.5, 128.4, 128.1, 126.7, 126.4, 126.3, 125.6, 33.1. MS: *m/z* (%) = 345 (51, M^+), 207 (49), 165 (33), 139 (35), 105 (42), 77 (100). Elemental Anal. Calcd for $C_{22}H_{16}ClNO$: calcd. C, 76.41; H, 4.66; N, 4.05. Found: C, 76.55; H, 4.82; N, 4.32.

*4.1.3.8. 4-Benzyl-2,5-bis(4-chlorophenyl)oxazole (**6h**).* white solid (0.59 g, 78%). mp. 157–158 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.03 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.57 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.45–7.23 (m, 9H, Ar-H), 4.18 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 159.1, 145.8, 138.1, 136.4, 136.3, 134.0, 129.1, 129.0, 128.7, 128.3, 127.6, 126.9, 126.7, 126.5, 125.7, 33.1. MS: *m/z* (%) = 379 (100, M^+), 241 (22), 207 (30), 139 (75), 111 (25). Elemental Anal. Calcd for $C_{22}H_{15}Cl_2NO$: C, 69.49; H, 3.98; N, 3.68. Found: C, 69.72; H, 4.91; N, 3.79.

*4.1.3.9. 4-Benzyl-5-(4-chlorophenyl)-2-(4-nitrophenyl)oxazole (**6i**).* yellow solid (0.56 g, 72%). mp. 207–209 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.33 (d, *J* = 7.8 Hz, 2H, Ar-H), 8.26 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.43 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.44–7.24 (m, 7H, Ar-H), 4.21 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 157.8, 148.5, 147.1, 137.8, 137.2, 134.6, 132.6, 129.7, 129.3, 128.7, 128.3, 127.0, 126.7, 126.5, 124.2, 33.1. MS: *m/z* (%) = 390 (100, M^+), 241 (29), 207 (47), 178 (46), 139 (48), 103 (47). Elemental Anal. Calcd for $C_{22}H_{15}ClN_2O_3$: C, 67.61; H, 3.87; N, 7.17. Found: C, 67.82; H, 4.11; N, 7.35.

*4.1.3.10. 4-Benzyl-2-(2-chlorophenyl)-5-(4-chlorophenyl)oxazole (**6j**).* white solid (0.52 g, 68%). mp. 116–118 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.09 (d, *J* = 6.6 Hz, 1H, Ar-H), 7.60 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.52–7.23 (m, 10H, Ar-H), 4.22 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 158.0, 146.0, 138.1, 135.8, 133.8, 132.2, 131.1, 130.9, 129.0, 128.6, 128.3, 126.9, 126.7, 126.6, 126.4, 125.9, 33.1. MS: *m/z* (%) = 379 (42, M^+), 241(26), 207 (26), 178 (38), 139 (100), 110 (57). Elemental Anal. Calcd for $C_{22}H_{15}Cl_2NO$: C, 69.49; H, 3.98; N, 3.68. Found: C, 69.42; H, 4.17; N, 3.62.

*4.1.3.11. 4-(4-Chlorobenzyl)-2-(4-chlorophenyl)-5-phenyloxazole (**6k**).* white solid (0.63 g, 83%). mp. 142–143 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.08 (d, *J* = 8.4 Hz, 1H, Ar-H), 8.03 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.63–7.25 (m, 10H, Ar-H), 4.16 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 159.0, 146.8, 141.4, 136.9, 136.4, 135.3, 132.2, 131.8, 129.7, 129.0, 128.7, 128.3, 127.6, 125.8, 125.6, 32.4. MS: *m/z* (%) = 379 (100, M^+), 207 (14), 178 (17), 165 (26), 139 (77), 77 (74). Elemental Anal. Calcd for $C_{22}H_{15}Cl_2NO$: C, 69.49; H, 3.98; N, 3.68. Found: C, 69.63; H, 4.05; N, 3.85.

*4.1.3.12. 4-(4-Chlorobenzyl)-2-(2-chlorophenyl)-5-phenyloxazole (**6l**).* white solid (0.58 g, 76%). mp. 124–125 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.08 (d, *J* = 9.0 Hz, 1H, Ar-H), 7.65 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.53–7.26 (m, 10H, Ar-H), 4.20 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 158.0, 147.1, 136.9, 134.9, 132.3, 132.2, 131.2, 130.9, 129.8, 128.9, 128.6, 128.3, 128.2, 126.8, 126.1, 125.6, 32.5. MS: *m/z* (%) = 379 (37, M^+), 207 (17), 178 (31), 165 (38), 105 (53), 77 (90). Elemental Anal. Calcd for $C_{22}H_{15}Cl_2NO$:C, 69.49; H, 3.98; N, 3.68. Found: C, 69.22; H, 3.77; N, 3.64.

*4.1.3.13. 4-(4-Chlorobenzyl)-2-(4-nitrophenyl)-5-phenyloxazole (**6m**).* yellow solid (0.56 g, 72%). mp. 184–185 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.33 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.26 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.66 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.49–7.26 (m, 7H, Ar-H), 4.19 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 157.7, 148.4, 148.1, 136.6, 136.3, 132.6, 132.4, 129.7, 129.0, 128.8, 128.7, 127.8, 126.9, 125.8, 124.1, 32.4. MS: *m/z* (%) = 390 (100, M^+), 207 (25), 178 (21), 105 (27), 77 (62). Elemental Anal. Calcd for $C_{22}H_{15}ClN_2O_3$: C, 67.61; H, 3.87; N, 7.17. Found: C, 67.82; H, 3.99; N, 6.98.

*4.1.3.14. 2-(4-Chlorophenyl)-4-(furan-2-ylmethyl)-5-phenyloxazole (**6n**).* light yellow solid (0.46 g, 69%). mp. 144–145 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.03 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.70 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.48–6.15 (m, 8H, Ar-H), 4.17 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 158.9, 151.9, 146.9, 141.6, 136.3, 133.4, 129.0, 128.9, 128.3, 128.2, 127.6, 127.4, 125.8, 110.4, 106.5, 26.7. MS: *m/z* (%) = 335 (62, M^+), 306 (29), 230 (14), 139 (47), 105 (100), 77 (82). Elemental Anal. Calcd for $C_{20}H_{14}ClNO_2$: C, 71.54; H, 4.20; N 4.17. Found: C, 71.25; H, 4.14; N, 4.39.

*4.1.3.15. 4-(Furan-2-ylmethyl)-2-(4-nitrophenyl)-5-phenyloxazole (**6o**).* yellow solid (0.42 g, 61%). mp. 158–160 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.32 (d, *J* = 7.8 Hz, 2H, Ar-H), 8.26 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.74 (d, *J* = 6.6 Hz, 2H, Ar-H), 7.50–6.17 (m, 8H, Ar-H, =CH), 4.20 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 157.6, 151.6, 148.4, 148.3, 141.8, 141.7, 134.3, 132.7, 128.9, 128.6, 127.8, 126.9, 126.1, 124.1, 110.4, 106.7, 26.7. MS: *m/z* (%) = 346 (100, M^+), 316 (43), 271 (15), 141 (14), 105 (59), 77 (59). Elemental Anal. Calcd for $C_{20}H_{14}N_2O_4$:C, 69.36; H, 4.07; N, 8.09. Found: C, 69.44; H, 4.33; N, 7.91.

*4.1.3.16. 4-Benzyl-2-methyl-5-phenyloxazole (**6p**).* light yellow oil (0.37 g, 74%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.57 (d, *J* = 6.0 Hz, 2H, Ar-H), 7.38–7.19 (m, 8H, Ar-H), 4.08 (s, 2H, CH_2), 2.47 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 159.9, 146.0, 138.6, 134.1, 128.7, 128.5, 128.3, 127.7, 126.3, 125.4, 125.3, 32.9, 14.4. MS: *m/z* (%) = 249 (100, M^+), 207 (61), 179 (26), 131 (10), 103 (17), 77 (30). Elemental Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.64; H, 6.26; N, 5.69.

*4.1.3.17. 4-(4-Chlorobenzyl)-2-methyl-5-phenyloxazole (**6q**).* light yellow oil (0.40 g, 71%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.54 (d, *J* = 6.6 Hz, 2H, Ar-H), 7.40 (d, *J* = 6.0 Hz, 2H, Ar-H), 7.32–7.19 (m, 9H, Ar-H), 4.04 (s, 2H, CH_2), 2.49 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 160.0, 146.1, 137.1, 133.6, 132.1, 129.7, 128.8, 128.7, 128.5, 127.9, 125.2, 32.2, 13.9. MS: *m/z* (%) = 283 (100, M^+), 241 (31), 207 (21), 178 (26), 105 (28), 77 (37). Elemental Anal. Calcd for $C_{17}H_{14}ClNO$: C, 71.96; H, 4.97; N, 4.94. Found: C, 71.78; H, 5.02; N, 5.17.

*4.1.3.18. 4-Benzyl-5-phenyl-2-propyloxazole (**6r**).* light yellow oil (0.44 g, 79%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.56 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.42–7.20 (m, 8H, Ar-H), 4.11 (s, 2H, CH_2), 2.78 (t, *J* = 7.2 Hz, 2H, CH_2), 1.86–1.82 (m, 2H, CH_2), 1.02 (t, *J* = 7.2 Hz, 2H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 163.3, 145.9, 138.7, 133.9, 128.9, 128.7, 128.5, 128.3, 127.6, 126.2, 125.3, 32.9, 30.1, 20.6, 13.4. MS: *m/z*

(%) = 277 (100, M^+), 249 (61), 207 (50), 179 (20), 103 (50), 77 (37). Elemental Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.43; H, 6.81; N, 5.16.

*4.1.3.19. 4-Benzyl-5-methyl-2-phenyloxazole (**6s**).* white solid (0.42 g, 84%). mp. 67–68 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.98 (d, J = 6.6 Hz, 2H, Ar-H) 7.41–7.19 (m, 8H, Ar-H), 3.88 (s, 2H, CH_2), 2.26 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 159.1, 139.0, 134.8, 129.4, 128.5, 128.4, 128.3, 127.6, 126.0, 125.8, 125.7, 32.0, 10.5. MS: m/z (%) = 249 (100, M^+), 206 (9), 145 (35), 131 (46), 105 (68), 77 (52). Elemental Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.79; H, 6.45; N, 5.54.

4.2. Spectroscopic measurements

All the solutions were prepared using spectroscopic grade solvents. Absorption spectra were recorded using a Scinco S-3100 UV-spectrophotometer. Fluorescence measurements were performed using a Fluoro Max-3-P spectrofluorimeter, equipped with double monochromators in both excitation and emission and a temperature controlled cuvette holder. Fluorescence spectra were corrected for the instrumental response of the system. The absorption and fluorescence spectra were recorded at 25 °C.

4.3. Fluorescence quantum yield

The fluorescence quantum yield (Φ_s) were determined using the standard method (Eq. (1))

$$\phi_s = \phi_r \frac{F_s A_r n_S^2}{F_r A_s n_S^2} \quad (1)$$

where A is the absorbance at the excitation wavelength, F is the integrated emission area and n is the refraction index of the solvents used. Subscripts refer to the reference (s) or sample (r) compound. Fluorescence quantum yields were relatively determined on the basis of phenol (Φ = 0.14 at 25 °C) for **6a**, **6p**, and on the basis of quinine sulphate (Φ = 0.577 at 25 °C) for **6d**, **6h**, **6l**, **6n**.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.12.040.

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