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Synthesis and photophysical properties of novel chloroquinoline based chalcone derivates containing 1,2,3-triazole moiety

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ABSTRACT

A series of novel chloroquinoline based chalcones containing 1,2,3-triazole moiety were synthesized. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, mass spectra and single crystal X-ray diffraction study. The absorbance, fluorescence spectra and quantum yield of all compounds were investigated in methanol. Photophysical properties of 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (3a) were investigated in detail. The effect of various solvents over emission spectra of 3a was studied using Kamlet–Taft and Catalan polarity scales. The quantum yield of 3a in various solvents was also recorded. The ground state and excited state dipole moments of compound 3a were determined using solvatochromic methods. The ground state dipole moment was estimated to be 1.081 D, while excited state dipole moment was found in the range of 11.969–3.801 D. Thermal stability of compound 3a and its precursor was also investigated using thermogravimetric analysis.

1. Introduction

Development of new fluorescent molecules has attracted much attention during the past few years due to their increasing applications in wide range of electronic and optoelectronic devices related to telecommunications, optical computing, optical storage and optical information processing [1]. Chalcones constitute an important class of naturally occurring flavonoids exhibiting a wide spectrum of biological activities [2,3]. Chalcone derivatives are also important due to their photophysical properties and optical applications such as second harmonic generation materials in non-linear optics [4], photorefractive polymers [5], holographic recording materials [6], fluorescent probes for sensing of metal ions [7] and microenvironment in micelles [8]. Photophysical and spectroscopic properties of chalcones can be readily modified by the introduction of conjugation. 1,2,3-triazoles are privileged structures and have found applications as fluorescent brighteners [9], dyes [10], corrosion-retarding agents [11] and fluorescent metal ion sensors [12]. Triazole derivatives have also been studied for their optical brightening properties [13,14]. Substituted quinoline derivatives have rigid structure, wide energy gaps, high fluorescent quantum yield and are widely used as fluorescence materials and sensors for metal ions and biological molecules [15]. The fluorescent characteristics of a molecule mainly depend on the molecular structure, such as conjugate system, coplanarity and rigidity. Thus there is a considerable interest to increase the conjugation in molecules in order to acquire favorable physical properties required for specific applications [16].

Hence, our approach was to design newly conjugated derivatives with fluorescent properties that can be used as fluorescent material with diverse applications. There is no report on the photophysical properties of triazole, chalcone and quinoline heterocyclic conjugates. Introduction of 1,2,3-triazole unit and quinoline moiety into the chalcone structure can significantly improve the photophysical properties of chalcones by increasing overall conjugation. Thus, in present work we report the synthesis and photophysical properties of a novel series of fluorescent chalcones derivatives containing 1,2,3-triazole and chloroquinoline moieties. Further solvatochromism [17], dipole moment [18] and thermal characteristics were also studied.

2. Experimental

All chemicals were purchased from Spectrochem India and were used as received. Precoated aluminum plates (Silica gel $60F_{254}$) from Merck were used to monitor reaction progress. IR (KBr) spectra were recorded on a PerkinElmer FTIR spectrophotometer and the values are expressed as ν_{max} cm^{-1}. The NMR (^{1}H and ^{13}C) spectra were recorded on Jeol JNM ECX-400P at 400 MHz and 100 MHz, respectively. The chemical shift values are

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recorded on δ scale and the coupling constants (J) are in Hertz. The mass spectra were recorded on an Agilent 6520-QTOF LCMS having ESI source in positive mode. X-ray intensity data was collected on an Oxford Diffraction Xcalibur CCD diffractometer with graphite monochromatic Mo Kα radiation (λ=0.71073 Å) at temperature 298 K. Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Center with CCDC no. 1013869. These data can be obtained free of charge from the CCDC *via* www.ccdc.cam.ac.uk/data_request/cif. Ultraviolet–visible (UV–vis) absorption spectra were recorded on an Analytikjena specord 250 spectrophotometer. The fluorescence spectra were measured on a Cary Eclipse Fluorescence spectrophotometer. The quantum yield (Φ) was measured by comparing the integrated photoluminescence intensities and the absorbance values with the reference fluorophore quinine sulfate (QS) according to Eq. (1), wherein Φ is the quantum yield, I is the measured integrated emission intensity, η is the refractive index, and A is the optical density. The subscript R refers to the reference fluorophore of known quantum yield

$$\Phi = \phi_R \frac{I A_R \eta^2}{I_R A \eta_R^2} \quad (1)$$

For all measurements, excitation wavelength was employed at 365 nm with slit width of 5 nm. The statistical calculations and linear fit were performed in Origin 7.0 program.

2.1. Procedure for synthesis of 4-azido-7-chloroquinoline (1)

A mixture of 4,7-dichloroquinoline (1.0 mmol), sodium azide (1.1 mmol) and PEG-400 (5 mL) was stirred at 60 °C for 1 h. The reaction was monitored by TLC (ethyl acetate–petroleum ether (40:60, v/v) as eluent). After completion of reaction as indicated by TLC, reaction mixture was allowed to cool to room temperature and water (20 mL) was added to reaction mixture. The precipitate formed was collected by filtration at a pump, and washed with water to afford crude product. The resulting product residue was crystallized from ethanol to yield the pure product 1 as colorless solid in 93% yield, m.pt 115–117 °C [19].

2.2. Procedure for the synthesis of 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)ethanone (2).

A mixture of 4-azido-7-chloroquinoline 1 (1.0 mmol) and acetylacetone (1.1 mmol) was placed in a 50 mL round-bottomed flask containing task specific basic ionic liquid [bmim]OH (10.0 mmol). The mixture was stirred at 80 °C for 15 min. After completion of the reaction as monitored by TLC using ethyl acetate:petroleum ether (70:30, v/v) as eluent, the reaction mixture was allowed to cool to room temperature and was quenched with water (10 mL). The precipitate formed was collected by filtration at a pump, washed with water and dried. The crude product was crystallized from ethanol to yield the pure 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)ethanone (2) as colorless solid in 92% yield.

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) 8.83 (d, 1H, J=4.9, ArH), 8.09 (d, 1H, J=2.4, ArH), 8.01 (d, 1H, J=9.3, ArH), 7.49 (m, 1H, ArH), 7.13 (d, 1H, J=4.9, ArH), 2.62 (s, 3H, $COCH_3$), 2.40 (s, 3H, CH_3); ^{13}C (100 MHz, $CDCl_3$) 190.26, 150.9, 149.1, 146.8, 141.20, 136.9, 131.45, 127.9, 123.8, 121.40, 119.9, 108.7, 27.56, 9.69; IR (KBr) ν_{max} cm^{-1}: 3021, 1656, 1612, 1560, 1435; MS (ESI) m/z calcd. for $C_{14}H_{11}ClN_4O$: 286.0621 found: 287.1201 (M^++1).

2.3. General procedure for synthesis of triazolyl chalcones (3a–3o)

A mixture of the substituted aromatic aldehyde (1.0 mmol) and 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl) ethanone (2) (1.0 mmol) dissolved in ethanol (10 mL) was added slowly to an aqueous solution of potassium hydroxide (1.2 mmol) in water (5 mL). The reaction mixture was stirred at 0 °C firstly for 10 min, and then at room temperature for 3–4 h. The progress of reaction was monitored by TLC using ethyl acetate–petroleum ether (60:40, v/v) as eluent. After completion of reaction as indicated by TLC, the reaction mixture was filtrated and the solid so obtained was washed with cold water. The crude product obtained was crystallized from ethanol to yield pure derivatives 3a–3o in good yield.

2.4. Spectral data for triazolyl chalcones 3a–3o

2.4.1. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (3a)

Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.14 (d, 1H, J=4.4 Hz, ArH), 8.28 (d, 1H, J=2.2 Hz, ArH), 8.00 (d, 1H, J=16.12 Hz, CH_a=CH), 7.89 (d, 1H, J=16.12 Hz, CH=CH_b), 7.58–7.56 (m, 1H, ArH), 7.43 (d, 1H, J=4.4 Hz, ArH), 7.35 (d, 1H, J=8.8 Hz, ArH), 6.95–6.94 (m, 2H, ArH), 3.95 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.84, 153.48, 151.31, 150.10, 144.60, 140.65, 140.15, 139.56, 138.26, 137.34, 131.08, 130.20, 129.88, 129.08, 123.75, 122.16, 121.76, 118.86, 106.01, 60.06, 56.28, 9.90; IR (KBr, cm^{-1}): ν_{max}=2926, 1665, 1605, 1578, 1502, 1416; MS (ESI) m/z calcd. for $C_{24}H_{21}ClN_4O_4$: 464.1251 found: 465.1568 (M^++1).

2.4.2. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (3b)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.12 (d, 1H, J=4.4 Hz, ArH), 8.27 (d, 1H, J=1.48 Hz, ArH), 7.99 (d, 1H, J=16.12 Hz, CH_a=CH), 7.93 (d, 1H, J=16.12 Hz, CH=CH_b), 7.69 (d, 2H, J=8.8 Hz, ArH), 7.55–7.58 (m, 1H, ArH), 7.43 (d, 1H, J=4.4 Hz, ArH), 7.34 (d, 1H, J=8.8 Hz, ArH), 6.94 (d, 1H, J=8.8 Hz, ArH), 3.85 (s, 3H, OCH_3), 2.53 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.93, 161.89, 151.35, 149.97, 144.23, 144.00, 139.83, 139.58, 137.26, 130.76, 129.88, 129.07, 127.50, 123.82, 122.26, 120.29, 118.79, 114.42, 55.14, 9.96; IR (KBr, cm^{-1}): ν_{max}=2927, 1661, 1590, 1511, 1423; MS (ESI) m/z calcd. for $C_{22}H_{17}ClN_4O_2$: 404.1040 found: 405.1091 (M^++1).

2.4.3. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(4-(trifluoromethyl)phenyl) prop-2-en-1-one (3c)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.13 (d, 1H, J=5.12 Hz, ArH), 8.27 (d, 1H, J=2.2 Hz, ArH), 8.16 (d, 1H, J=16.12 Hz, CH_a=CH), 7.94 (d, 1H, J=16.12 Hz, CH=CH_b), 7.82 (d, 2H, J=8.08 Hz, ArH), 7.67 (d, 1H, J=8.08 Hz, ArH), 7.55–7.58 (m, 1H, ArH), 7.43 (d, 1H, J=4.4 Hz, ArH), 7.32 (d, 1H, J=8.8 Hz, ArH), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.62, 151.36, 150.03, 143.68, 142.20, 140.38, 139.32, 138.05, 137.27, 131.84, 129.92, 129.17, 128.83, 125.89, 125.85, 124.79, 123.66, 122.12, 118.76, 9.96; IR (KBr, cm^{-1}): ν_{max}=2926, 1669, 1609, 1431,1309; MS (ESI) m/z calcd. for $C_{22}H_{14}ClF_3N_4O$: 442.0808 found: 443.1201 (M^++1).

2.4.4. 4-(3-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-oxoprop-1-enyl) benzonitrile (3d)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.13 (d, 1H, J=4.4 Hz, ArH), 8.28 (d, 1H, J=1.48 Hz, ArH), 8.16 (d, 1H, J=16.12 Hz, CH_a=CH), 7.91 (d, 1H, J=16.12 Hz, CH=CH_b), 7.80 (d, 2H, J=8.8 Hz, ArH), 7.71 (d, 2H, J=8.8 Hz, ArH), 7.56–7.58 (m, 1H, ArH), 7.43 (d, 1H, J=4.4 Hz, ArH), 7.31 (d, 1H, J=9.52 Hz, ArH), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.45, 151.38, 150.05, 143.67, 141.59, 140.53, 139.31, 139.02, 137.36, 132.69, 129.99, 129.21, 129.03, 125.71, 123.63, 122.12, 118.78, 113.65, 10.00; IR (KBr, cm^{-1}): ν_{max}=2925, 1667, 1611, 1560, 1429; MS (ESI) m/z calcd. for $C_{22}H_{14}ClN_5O$: 399.0887 found: 400.1024 (M^++1).

2.4.5. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-p-tolylprop-2-en-1-one (3e)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.14 (d, 1H, J=4.4 Hz, ArH), 8.28 (d, 1H, J=1.06 Hz, ArH), 8.08 (d, 1H, J=16.12 Hz, CH_a=CH), 7.95 (d, 1H, J=16.12 Hz, CH=CH_b), 7.64 (d, 2H, J=8.8 Hz, ArH), 7.56–7.59 (m, 1H, ArH), 7.44 (d, 1H, J=4.4 Hz, ArH), 7.35 (d, 1H, J=8.8 Hz, ArH), 7.25 (d, 1H, J=2.2 Hz, ArH), 2.54 (s, 3H, OCH_3), 2.40 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.14, 151.37, 150.01, 144.52, 143.95, 141.41, 140.02, 139.50, 137.26, 131.99, 128.89, 129.70, 129.10, 128.89, 123.79, 122.23, 121.58, 118.79, 21.57, 9.98; IR (KBr, cm^{-1}): ν_{max}=2920, 1664, 1598, 1560, 1435; MS (ESI) *m/z* calcd. for $C_{22}H_{17}ClN_4O$: 388.1091 found: 389.1201 (M^++1).

2.4.6. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(3-nitrophenyl)prop-2-en-1-one (3f)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.14 (d, 1H, J=4.4 Hz, ArH), 8.55 (d, 1H, J=2.2 Hz, ArH), 8.24–8.28 (m, 2H, ArH), 8.20 (d, 1H, J=16.12 Hz, CH_a=CH), 8.02 (d, 2H, J=8.04 Hz, ArH), 7.96 (d, 1H, J=16.12 Hz, CH=CH_b), 7.56–7.64 (m, 2H, ArH), 7.43 (d, 2H, J=4.4 Hz, ArH), 7.43 (d, 1H, J=4.4 Hz, ArH), 7.32 (d, 1H, J=8.76 Hz, ArH), 2.55 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.42, 151.38, 150.06, 148.75, 143.62, 141.23, 140.52, 139.33, 137.36, 136.51, 134.13, 130.00, 129.20, 125.34, 124.87, 123.65, 123.16, 122.14, 118.78, 10.01; IR (KBr, cm^{-1}): ν_{max}=3075, 1670, 1610, 1553, 1431; MS (ESI) *m/z* calcd. for $C_{21}H_{14}ClN_5O_3$: 419.0785 found: 420.2365 (M^++1).

2.4.7. 3-(4-bromophenyl)-1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)prop-2-en-1-one (3g)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.13 (d, 1H, J=4.4 Hz, ArH), 8.28 (d, 1H, J=1.48 Hz, ArH), 8.16 (d, 1H, J=16.12 Hz, CH_a=CH), 7.91 (d, 1H, J=16.12 Hz, CH=CH_b), 7.80 (d, 2H, J=8.8 Hz, ArH), 7.71 (d, 2H, J=8.8 Hz, ArH), 7.56–7.58 (m, 1H, ArH), 7.43 (d, 1H, J=4.4 Hz, ArH), 7.31 (d, 1H, J=9.52 Hz, ArH), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.45, 151.38, 150.05, 143.67, 141.59, 140.53, 139.31, 139.02, 137.36, 132.69, 129.99, 129.21, 129.03, 125.71, 123.63, 122.12, 118.78, 113.65, 10.00; IR (KBr, cm^{-1}): ν_{max}=2925, 1664, 1602, 1560, 1432; MS (ESI) *m/z* calcd. for $C_{21}H_{14}BrClN_4O$: 452.0040 found: 454.1985 (M^++2).

2.4.8. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (3h)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.13 (d, 1H, J=4.4 Hz, ArH), 8.28 (d, 1H, J=1.48 Hz, ArH), 8.16 (d, 1H, J=16.12 Hz, CH_a=CH), 7.91 (d, 1H, J=16.12 Hz, CH=CH_b), 7.80 (d, 2H, J=8.8 Hz, ArH), 7.71 (d, 2H, J=8.8 Hz, ArH), 7.56–7.58 (m, 1H, ArH), 7.43 (d, 1H, J=4.4 Hz, ArH), 7.31 (d, 1H, J=9.52 Hz, ArH), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.45, 151.38, 150.05, 143.67, 141.59, 140.53, 139.31, 139.02, 137.36, 132.69, 129.99, 129.21, 129.03, 125.71, 123.63, 122.12, 118.78, 113.65, 10.00; IR (KBr, cm^{-1}): ν_{max}=2970, 1670, 1545, 1425; MS (ESI) *m/z* calcd. for $C_{23}H_{19}ClN_4O_3$: 434.1146 found: 435.1258 (M^++1).

2.4.9. 3-(4-chlorophenyl)-1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)prop-2-en-1-one (3i)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.14 (d, 1H, J=3.68 Hz, ArH), 8.27 (s, 1H, ArH), 8.07 (d, 1H, J=16.12 Hz, CH_a=CH), 7.89 (d, 1H, J=16.12 Hz, CH=CH_b), 7.65 (d, 2H, J=8.08 Hz, ArH), 7.56 (d, 1H, J=8.04 Hz, ArH), 7.31–7.43 (m, 4H, ArH), 2.53 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.82, 151.38, 150.06, 143.80, 142.83, 140.22, 139.43, 137.29, 136.69, 133.23, 129.96, 129.93, 129.25, 129.18, 123.72, 123.06, 122.18, 118.78, 9.99; IR (KBr, cm^{-1}): ν_{max}=2925, 1665, 1603, 1560, 1436; MS (ESI) *m/z* calcd. for $C_{21}H_{14}Cl_2N_4O$: 408.0545 found: 409.0820 (M^++1).

2.4.10. 3-(benzo[d][1,3]dioxol-5-yl)-1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)prop-2-en-1-one (3j)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.11 (d, 1H, J=5.16 Hz, ArH), 8.27 (d, 1H, J=2.2 Hz, ArH), 7.98 (d, 1H, J=16.12 Hz, CH_a=CH), 7.88 (d, 1H, J=16.12 Hz, CH=CH_b), 7.56 (d, 1H, J=7.32 Hz, ArH), 7.44–7.32 (m, 3H, ArH), 6.96–6.94 (m, 2H, ArH), 6.04 (s, 2H, OCH_2), 2.53 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.91, 151.36, 150.13, 150.02, 148.43, 144.19, 143.93, 139.93, 139.49, 137.22, 129.85, 129.42, 129.11, 125.71, 123.78, 122.21, 120.69, 118.78, 108.61, 107.01, 101.64, 9.95; IR (KBr, cm^{-1}): ν_{max}=2924, 1660, 1592, 1498, 1448; MS (ESI) *m/z* calcd. for $C_{22}H_{15}ClN_4O_3$: 418.0833 found: 419.1120 (M^++1).

2.4.11. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(furan-2-yl)prop-2-en-1-one (3k)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.13 (d, 1H, J=4.4 Hz, ArH), 8.27 (d, 1H, J=2.2 Hz, ArH), 7.94 (d, 1H, J=16.12 Hz, CH_a=CH), 7.73 (d, 1H, J=15.4 Hz, CH=CH_b), 7.58–7.55 (m, 2H, ArH), 7.41 (d, 1H, J=5.12 Hz, ArH), 7.33 (d, 1H, J=9.56 Hz, ArH), 6.79 (d, 1H, J=2.92 Hz, ArH), 6.52–6.51 (m, 1H, ArH), 2.52 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.97, 151.72, 151.39, 149.95, 145.37, 143.91, 139.94, 139.53, 137.27, 130.33, 129.89, 129.14, 123.82, 122.26, 120.50, 118.79, 116.65, 112.71, 9.98; IR (KBr, cm^{-1}): ν_{max}=2925, 1667, 1609, 1533, 1431; MS (ESI) *m/z* calcd. for $C_{19}H_{13}ClN_4O_2$: 364.0727 found: 365.1254 (M^++1).

2.4.12. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(3,5-dichlorophenyl)prop-2-en-1-one (3l)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.14 (d, 1H, J=4.4 Hz, ArH), 8.28–8.27 (m, 2H, ArH), 8.05 (d, 1H, J=16.12 Hz, CH_a=CH), 7.84 (d, 1H, J=8.08 Hz, CH=CH_b), 7.59–7.56 (m, 1H, ArH), 7.47 (d, 1H, J=2.2 Hz, ArH), 7.42 (d, 1H, J=4.4 Hz, ArH), 7.33–7.30 (m, 2H, ArH), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.55, 151.36, 150.03, 143.37, 142.35, 140.41, 139.37, 138.69, 137.28, 136.79, 136.44, 131.57, 130.11, 129.99, 129.18, 128.69, 127.63, 125.10, 123.70, 118.78, 9.74; IR (KBr, cm^{-1}): ν_{max}=2925, 1666, 1604, 1466, 1431; MS (ESI) *m/z* calcd. for $C_{21}H_{13}Cl_3N_4O_2$: 442.0155 found: 443.0253 (M^++1).

2.4.13. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(4-fluorophenyl)prop-2-en-1-one (3m)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.13 (d, 1H, J=4.4 Hz, ArH), 8.28–8.27 (m, 2H, ArH), 8.03 (d, 1H, J=16.12 Hz, CH_a=CH), 7.91 (d, 1H, J=16.12 Hz, CH=CH_b), 7.74–7.70 (m, 2H, ArH), 7.58–7.55 (m, 1H, ArH), 7.42 (d, 1H, J=5.16 Hz, ArH), 7.33 (d, 1H, J=8.8 Hz, ArH), 7.13–7.09 (t, 2H, J=8.8 Hz, ArH), 2.53 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.88, 151.36, 150.02, 143.82, 143.02, 140.15, 139.45, 137.28, 130.98, 130.80, 130.71, 129.91, 129.13, 123.72, 123.34, 122.34, 118.78, 116.24, 9.97; IR (KBr, cm^{-1}): ν_{max}=2936, 1665, 1610, 1596, 1503, 1420; MS (ESI) *m/z* calcd. for $C_{21}H_{14}ClN_4O$: 392.0840 found: 393.1450 (M^++1).

2.4.14. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(4-(dimethylamino) phenyl) prop-2-en-1-one (3n)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.13 (d, 1H, J=4.4 Hz, ArH), 8.27–8.27 (m, 2H, ArH), 7.94 (d, 1H, J=16.12 Hz, CH_a=CH), 7.89 (d, 1H, J=15.36 Hz, CH=CH_b), 7.63 (d, 2H, J=8.8 Hz, ArH), 7.57–7.54 (m, 1H, ArH), 7.42 (d, 1H, J=5.12 Hz, ArH), 7.35 (d, 1H, J=9.52 Hz, ArH), 6.69 (d, 1H, J=8.76 Hz, ArH), 3.04 (s, 6H, $N(CH_3)_2$), 2.53 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.00, 151.35, 151.24, 141.69, 141.51, 139.37, 137.33, 137.24, 135.19, 131.81, 131.56, 131.10, 129.95, 129.80, 129.58, 129.27, 128.78, 128.46, 127.16, 126.49, 125.74, 125.60, 125.41, 125.20, 123.79, 123.69, 123.59, 9.95; IR (KBr, cm^{-1}): ν_{max}=2922, 1654, 1570, 1524, 1432;

MS (ESI) *m/z* calcd. for $C_{29}H_{19}ClN_4O$: 474.1247 found: 475.1356 ($M^+ + 1$).

2.4.15. 3-(anthracen-9-yl)-1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)prop-2-en-1-one (3o)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.14 (d, 1H, J=4.4 Hz, ArH), 8.98–8.96 (m, 1H, ArH), 8.48–8.28 (m, 4H, ArH), 8.06–8.02 (m, 3H, ArH), 7.59–7.35 (m, 6H, ArH), 2.62 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.02, 152.31, 151.39, 150.04, 145.37, 144.14, 139.68, 139.58, 137.19, 130.92, 129.88, 129.08, 123.92, 122.59, 122.33, 118.81, 117.34, 111.78, 40.12, 9.98; IR (KBr, cm^{-1}): ν_{max}=2921, 1670, 1611, 1554, 1428; MS (ESI) *m/z* calcd. for $C_{231}H_{20}ClN_5O$: 417.1356 found: 418.1589 ($M^+ + 1$).

2.5. Procedure for the synthesis of 4-(3-chloropropoxy)benzaldehyde (4)

A mixture of 4-hydroxybenzaldehyde (1.0 mmol), 1-bromo-3-chloropropane (1.1 mmol) and K_2CO_3 (2.5 mmol) in PEG-400 (10 mL) was stirred at 80 °C for 1 h. After completion of the reaction as indicated by TLC using ethyl acetate:petroleum ether (30:70, v/v) as eluent, the reaction mixture was allowed to cool to room temperature and water (20 mL) was added to the reaction mixture. The reaction mixture was then extracted with ethylacetate (3 × 10 mL). The combined ethylacetate extracts were washed with 1 M HCl (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and saturated brine (2 × 10 mL). The filtrate was dried over $MgSO_4$ and filtered. The filtrate was evaporated to dryness *in vacuo* to give the product as yellow oil [20] in 94% yield.

2.6. Procedure for the synthesis of 3-(4-(3-chloropropoxy)phenyl)-1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)prop-2-en-1-one (5).

A mixture of 4-(3-chloropropoxy)benzaldehyde (4) (1.0 mmol) and 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl) ethanone (2) (1.0 mmol) dissolved in ethanol (10 mL) was added slowly to an aqueous solution of potassium hydroxide (1.2 mmol) in water (5 mL). The reaction mixture was stirred at 0 °C firstly for 10 min, and then at room temperature for 4 h. The progress of reaction was monitored by TLC using ethyl acetate:petroleum ether (60:40, v/v) as eluent. After completion of reaction as indicated by TLC, the reaction mixture was filtered and the solid was washed with cold water and cold ethanol. The crude product obtained was crystallized from ethanol to yield pure 3-(4-(3-chloropropoxy)phenyl)-1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)prop-2-en-1-one (5) in 94% yield.

Colorless solid; m.pt 157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.12 (d, 1H, J=4.14 Hz, ArH), 8.27 (m, 1H, ArH), 7.97 (d, 1H, J=16.12 Hz, CH_a=CH), 7.90 (d, 1H, J=16.12 Hz, CH=CH_b), 7.64 (d, 2H, J=7.54 Hz, ArH), 7.43–7.32 (m, 3H, ArH), 6.90 (d, 2H, J=8.18 Hz, ArH), 4.07–4.03 (t, 2H, J=6.04 Hz, OCH_2), 3.42–3.39 (t, 2H, J=5.96 Hz, $ClCH_2$), 2.43 (s, 3H, CH_3), 2.01–1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.15, 160.25, 149.24, 148.42, 141.94, 140.85, 139.78, 138.56, 134.30, 132.45, 129.54, 129.02, 126.61, 123.78, 121.87, 119.12, 117.56, 60.12, 52.23, 25.45, 9.90; IR (KBr, cm^{-1}): ν_{max}=2930, 1617, 1597, 1540, 1436; MS (ESI) *m/z* calcd. for $C_{24}H_{20}Cl_2N_4O_2$: 466.0963 found: 467.1025 ($M^+ + 1$).

2.7. General procedure for synthesis of 7-chloroquinoline linked triazolyl chalcone derivatives (6a–6f)

A mixture of 3-(4-(3-chloropropoxy)phenyl)-1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)prop-2-en-1-one (5) (1.0 mmol), various amines such as morpholine or piperidine or 2-(piperazin-1-yl)pyrimidine/N-methylpiperazine/N-acetylpiperazine/2-aminothiazole (1.1 mmol), KI (2.5 mmol) and DMF (10 mL) was placed in a 50 mL round-bottomed flask and stirred vigorously for 5–6 h at 110 °C. After the completion of reaction as evident by TLC using ethyl acetate–petroleum ether (80: 20, v/v) as eluent, the reaction mixture was allowed to cool at room temperature and poured on crushed ice. A solid separated out after a while. The solid was filtered at a pump, washed with water and dried under vacuum. The product obtained was further purified using flash column chromatography to yield pure derivatives 6a–6e.

2.8. Spectral data compounds of 6a–6e.

2.8.1. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(4-(3-morpholinopropoxy)phenyl)prop-2-en-1-one (6a)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.12 (d, 1H, J=4.04 Hz, ArH), 8.27 (s, 1H, ArH), 7.99 (d, 1H, J=16.08 Hz, CH_a=CH), 7.92 (d, 1H, J=16.12 Hz, CH=CH_b), 7.68 (d, 2H, J=8.76 Hz, ArH), 7.57–7.52 (m, 1H, ArH), 7.43–7.32 (m, 2H, ArH), 6.93 (d, 2H, J=8.08 Hz, ArH), 4.08–4.05 (t, 2H, J=5.88 Hz, OCH_2), 3.72–3.69 (m, 4H), 2.53 (s, 3H, CH_3), 2.50–2.45 (m, 6H), 2.01–1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.05, 161.39, 151.38, 150.01, 144.24, 143.87, 139.90, 139.34, 137.22, 130.68, 129.37, 129.11, 127.39, 123.80, 122.23, 120.20, 118.79, 114.89, 66.93, 66.22, 55.40, 53.69, 26.28, 9.99; IR (KBr, cm^{-1}): ν_{max}=2921, 1670, 1611, 1554, 1428; MS (ESI) *m/z* calcd. for $C_{28}H_{28}ClN_5O_3$: 517.1881 found: 517.2145 ($M^+ + 1$).

2.8.2. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(4-(3-(piperidin-1-yl)propoxy)phenyl)prop-2-en-1-one (6b)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.13 (d, 1H, J=4.4 Hz, ArH), 8.26 (s, 1H, ArH), 7.98 (d, 1H, J=15.4 Hz, CH_a=CH), 7.90 (d, 1H, J=15.4 Hz, CH=CH_b), 7.67 (d, 2H, J=8.76 Hz, ArH), 7.57–7.55 (m, 1H, ArH), 7.43–7.32 (m, 2H, ArH), 6.90 (d, 2H, J=8.8 Hz, ArH), 4.11–4.09 (t, 2H, J=5.88 Hz, OCH_2), 3.02–2.98 (m, 6H), 2.53 (s, 3H, CH_3), 2.39–2.34 (m, 2H), 1.26–1.21 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.97, 160.58, 151.38, 149.99, 143.96, 139.98, 139.48, 137.34, 130.69, 129.86, 129.10, 127.89, 123.77, 120.54, 118.79, 114.79, 113.96, 65.47, 55.47, 53.85, 29.65, 24.59, 23.37, 22.50, 9.98; IR (KBr, cm^{-1}): ν_{max}=2953, 1669, 1595, 1509, 1424; MS (ESI) *m/z* calcd. for $C_{29}H_{30}ClN_5O_2$: 515.2088 found: 516.2158 ($M^+ + 1$).

2.8.3. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(4-(3-(4-(pyrimidin-2-yl)piperazin-1-yl)propoxy)phenyl)prop-2-en-1-one (6c)

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.13 (d, 1H, J=4.4 Hz, ArH), 8.29–8.26 (m, 3H, ArH), 7.99 (d, 1H, J=16.08 Hz, CH_a=CH), 7.92 (d, 1H, J=15.36 Hz, CH=CH_b), 7.69–7.67 (m, 2H, ArH), 7.57–7.55 (m, 1H, ArH), 7.43–7.32 (m, 3H, ArH), 6.92 (d, 2H, J=2.2 Hz, ArH), 4.11–4.08 (t, 2H, J=5.88 Hz, OCH_2), 3.82–3.81 (m, 4H), 2.58–2.45 (m, 9H), 2.01–1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.02, 161.61, 161.36, 157.68, 151.37, 150.05, 144.25, 144.01, 139.88, 139.53, 137.22, 130.67, 129.85, 129.11, 127.42, 123.81, 122.25, 120.24, 118.79, 114.92, 109.82, 66.32, 50.05, 53.11, 43.68, 26.59, 9.97; IR (KBr, cm^{-1}): ν_{max}=2924, 1661, 1593, 1571, 1511, 1458; MS (ESI) *m/z* calcd. for $C_{32}H_{31}ClN_8O_2$: 594.2258 found: 595.3125 ($M^+ + 1$).

2.8.4. 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)-3-(4-(3-(4-methylpiperazin-1-yl)propoxy)phenyl)prop-2-en-1-one (6d)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.13 (d, 1H, J=4.4 Hz, ArH), 8.27–8.26 (m, 1H, ArH), 7.98 (d, 1H, J=16.08 Hz,

CH_a═CH), 7.92 (d, 1H, J=16.12 Hz, CH═CH_b), 7.67 (d, 2H, J=8.8 Hz, ArH), 7.57–7.54 (m, 1H, ArH), 7.41 (d, 1H, J=4.36 Hz, ArH), 7.33 (d, 1H, J=8.8 Hz, ArH), 6.92 (d, 2H, J=8.76 Hz, ArH), 4.07–4.04 (t, 2H, J=6.96 Hz, OCH_2), 2.57–2.53 (m, 13H), 2.33 (s, 3H, CH_3), 2.02–1.95 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.01, 161.35, 151.36, 150.02, 144.24, 144.00, 139.87, 139.51, 137.22, 130.66, 129.85, 129.10, 127.39, 123.79, 122.23, 120.25, 118.78, 114.90, 66.34, 54.94, 52.96, 45.84, 29.65, 26.85, 9.96; IR (KBr, cm^{-1}): ν_{max}=2925, 1660, 1589, 1560, 1436; MS (ESI) m/z calcd. for $C_{30}H_{31}ClN_6O_3$: 558.2146 found: 559.2569 (M^++1).

2.8.5. 3-(4-(3-(4-acetylpiperazin-1-yl)propoxy)phenyl)-1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)prop-2-en-1-one (6e)

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 9.13 (d, 1H, J=4.4 Hz, ArH), 8.27–8.26 (m, 1H, ArH), 7.99 (d, 1H, J=16.08 Hz, CH_a═CH), 7.91 (d, 1H, J=16.12 Hz, CH═CH_b), 7.66 (d, 2H, J=8.8 Hz, ArH), 7.57–7.54 (m, 1H, ArH), 7.41 (d, 2H, J=5.12 Hz, ArH), 7.33 (d, 2H, J=9.52 Hz, ArH), 6.92 (d, 2H, J=8.76 Hz, ArH), 4.08–4.04 (t, 2H, J=6.6 Hz, OCH_2), 3.59–3.61 (m, 2H), 3.46–3.44 (m, 2H), 2.53–2.38 (m, 9H), 1.99–1.96 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.97, 168.88, 161.24, 151.36, 149.98, 144.16, 143.96, 139.89, 139.48, 137.20, 130.66, 129.84, 129.08, 127.44, 123.77, 122.20, 120.22, 118.78, 114.85, 66.06, 54.78, 53.33, 52.70, 46.20, 41.31, 26.47, 21.30, 9.96; IR (KBr, cm^{-1}): ν_{max}=2924, 1664, 1597, 1444; MS (ESI) m/z calcd. for $C_{30}H_{31}ClN_6O_3$: 558.2146 found: 559.2569 (M^++1).

3. Result and discussion

We report herein synthesis of a series of new chloroquinoline based chalcone derivative containing a 1,2,3-triazole moiety (3a–3o). The compounds were synthesized by 1,3-dipolar cycloaddition of 4-azido-7-chloroquinoline to acetylacetone in the presence of [bmim]OH which serve as a catalyst and medium at 80 °C followed by condensation with different aromatic aldehydes in the presence of base as outlined in Scheme 1. Initially, 4-azido-7-chloroquinoline (1) was synthesized in 93% yield by the reaction of commercially available 4,7-dichloroquinoline with 1.1 eq. of sodium azide in PEG-400 at 60 °C for 1 h. 4-azido-7-chloroquinoline (1) was then converted to 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)ethanone (2) by 1,3-dipolar cycloaddition reaction with 1.1 eq. of acetylacetone in the presence of basic task specific ionic liquid bmim[OH] at 80 °C [21]. The product 2 was obtained in 92% yield after a simple workup.

The chalcone derivatives 3a–3o were then synthesized by Claisen–Schmidt aldol condensation reaction of 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)ethanone (2) with substituted aldehydes in the presence of 1.5 eq. of aq. KOH in ethanol by stirring the reaction mixture firstly at 0 °C for 10 min and then at room temperature for 3–4 h to give compounds 3a–3o (entry 1–15) in good yields as shown in Table 1.

Table 1
Synthesis of 7-chloroquinoline linked triazolyl–chalcones (3a–3o).

Entry	Ar	Product	Yield (%)	M. pt (°C)
1	3,4,5-$(CH_3O)_3C_6H_2$	3a	92	160–162
2	4-$MeOC_6H_4$	3b	89	120–122
3	4-$CF_3C_6H_4$	3c	88	164–167
4	4-CNC_6H_4	3d	89	233–236
5	4-MeC_6H_4	3e	93	193–196
6	3-$NO_2C_6H_4$	3f	95	142–145
7	4-BrC_6H_4	3g	90	191–193
8	3,4-$(CH_3O)_2C_6H_3$	3h	85	192–194
9	4-ClC_6H_4	3i	87	213–215
10	1-Piperonyl	3j	90	170–173
11	2-Furanyl	3k	91	150–153
12	3,5-$(Cl)_2C_6H_3$	3l	89	149–153
13	4-FC_6H_4	3m	88	201–205
14	4-$N(CH_3)_2C_6H_4$	3n	91	184–187
15	9-anthryl	3o	93	160–164

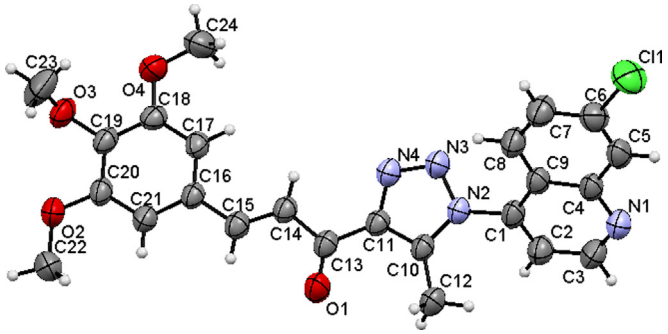
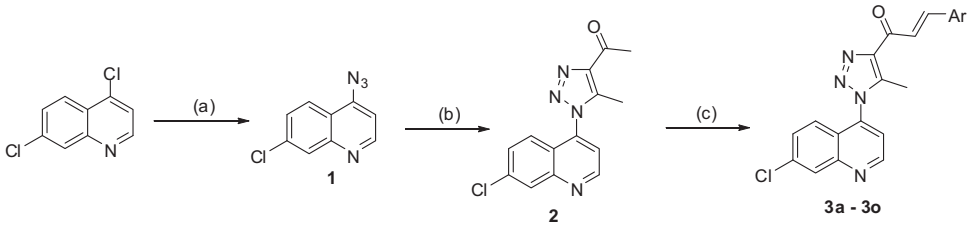


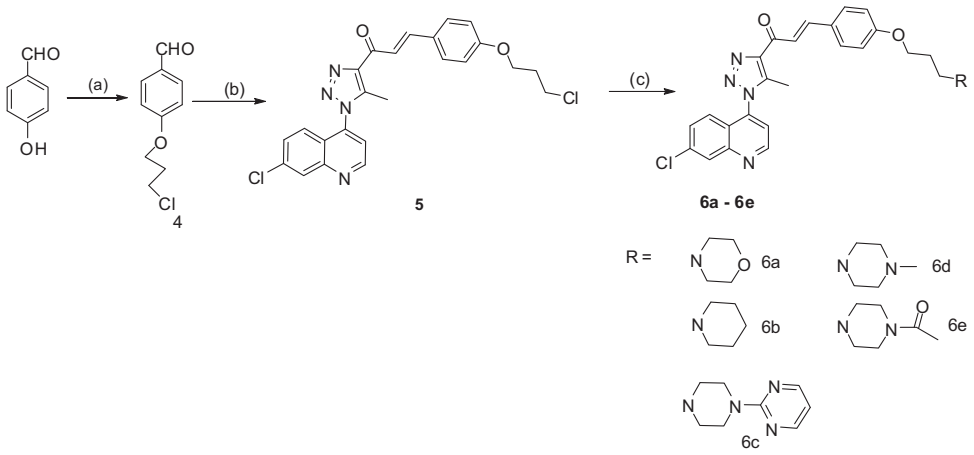
Fig. 1. Ortep diagram of the compound 3a drawn in 30% thermal probability ellipsoids.

Table 2
Summary of crystal data for compound 3a.

Identification code	Shelxl
Empirical formula	$C_{24}H_{21}ClN_4O_4$
Formula weight	464.12
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a=9.8641(7) Å, α=90.827(5)°. b=10.0762(6) Å, β=95.619(5)°. c=12.1716(8) Å, γ=100.318(5)°.
Volume	1183.85(13) Å^3
Z, density (calculated)	2, 1.304 Mg/m^3
Absorption coefficient	0.199 mm^{-1}
F (0 0 0)	484
Theta range for data collection	3.07–25.00°.
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 11$, $0 \le l \le 14$
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2$sigma(I)]	$R1$=0.0596, w$R2$=0.1569
R indices (all data)	$R1$=0.0877, w$R2$=0.1761



Scheme 1. Synthesis of 7-chloroquinoline linked triazolyl chalcones. Reagents and conditions: (a) NaN_3, PEG-400, 60 °C, 1 h; (b) acetylacetone, [bmim]OH (20 mol%), 20 min, 80 °C; (c) ArCHO, KOH, ethanol, 3–4 h, 0 °C–rt.



Scheme 2. Synthesis of 7-chloroquinoline linked triazolyl chalcone derivatives. Reagents and conditions: (a) 1-bromo-3-chloropropane, K_2CO_3, PEG-400, 80 °C, 1 h; (b) 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)ethanone, KOH, ethanol, 4 h, 0 °C–rt; (c) various amines, KI, DMF, 110 °C, 4 h.

Table 3
Synthesis of 7-chloroquinoline linked triazolyl–chalcone derivatives (6a–6e).

Entry	*R*	Product	Yield (%)	M. pt (°C)
1	Morpholine	6a	84	140
2	Piperidine	6b	90	186
3	2-(piperazin-yl)pyrimidine	6c	89	220
4	N-methylpiperazine	6d	87	205
5	N-acetylpiperazine	6e	91	174

Table 4
Photophysical data of all compounds (3a–3o, 6a–6e) in methanol.

Product	λ_{abs} (nm)	$\varepsilon \times 10^5$ (L mol^{-1} cm^{-1})	λ_{em} (nm)	Stoke shift ($\Delta\nu$) cm^{-1}	Quantum yield (Φ)
3a	235, 270, 345	0.87, 0.80, 0.35	524	10,415	0.059
3b	233, 300	0.98, 0.75	463	11,735	0.008
3c	236, 274, 344	0.85, 0.37, 0.40	–	–	–
3d	235, 322	0.80, 0.47	–	–	–
3e	234, 279	0.24, 0.22	411	11,512	0.010
3f	233, 293	0.64, 0.38	–	–	–
3g	235, 279, 319	0.75, 0.52, 0.46	–	–	–
3h	236, 269, 362	0.76, 0.49, 0.33	517	8282	0.084
3i	235, 316	0.77, 0.50	–	–	–
3j	236, 274, 364	0.97, 1.56, 0.32	–	–	–
3k	234, 274, 344	1.33, 0.52, 0.83	537	10,448	0.046
3l	236, 292	0.71, 0.44	–	–	–
3m	237, 275	0.61, 0.68	–	–	–
3n	237, 272, 423	0.92, 0.85, 0.61	534	4914	0.015
3o	395	0.075	481	4526	0.142
6a	237, 275, 345	0.95, 0.81, 0.34	464	7435	0.026
6b	239, 277, 352	0.31, 0.25, 0.058	476	7401	0.130
6c	237, 276, 347	0.98, 0.42, 0.50	462	7173	0.018
6d	236, 273, 346	0.62, 0.64, 0.22	461	7210	0.044
6e	238, 273, 347	0.65, 0.75, 0.17	468	7451	0.076

All the products were characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectra. The structure of 3a has also been confirmed by X-ray crystallography. The ORTEP diagram is shown below (Fig. 1) and crystal data is summarized in Table 2.

Another series of novel 1,2,3-triazolyl-chalcone derivatives were synthesized according to Scheme 2. Firstly 4-(3-chloropropoxy)benzaldehyde (4) was prepared by the reaction of 4-hydroxybenzaldehyde with 1.2 eq. of 1-bromo-3-chloropropane in the presence of K_2CO_3 in PEG-400 at 80 °C. The product 4 was obtained in 94% yield after 1 h. Claisen–Schmidt condensation of 4-(3-chloropropoxy) benzaldehyde (4) with 1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl) ethanone (2) in the presence of 1.5 eq. of aq. KOH in ethanol at 0 °C for 10 min and subsequently at room temperature for 4 h, yielded 91% of 3-(4-(3-chloropropoxy)phenyl)-1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)prop-2-en-1-one (5). Finally 7-chloroquinoline linked triazolyl–chalcones (6a–6e) were synthesized by the reaction of 3-(4-(3-chloropropoxy)phenyl)-1-(1-(7-chloroquinolin-4-yl)-5-methyl-1H-1,2,3-triazol-4-yl)prop-2-en-1-one (5) with various amines such as morpholine, piperidine, 2-(piperazin-1-yl)pyrimidine, N-methylpiperazine and N-acetylpiperazine in the presence of 2.5 eq. of KI in DMF at 110 °C for 5–6 h. The crude products were further purified by flash column chromatography to yield pure 6a–6e in high yields as listed in Table 3. Structures of all new compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. All triazolyl–chalcone derivatives (3a–3o, 6a–6e) exist in s-cis conformation as conformed by the X-ray crystal structure of compound 3a as shown in Fig. 1. This is also supported by IR and NMR data of all compounds. Carbonyl group starching in chalcone derivatives with s-cis conformation absorbs at higher frequency in IR as compared to s-trans conformation. All triazolyl–chalcone derivates (3a–3o, 6a–6e) showed single absorption for carbonyl group in the range of 1670–1660 cm^{-1}, which confirms that all triazolyl–chalcone derivatives exists in a s-cis conformation. The ^{1}H NMR data of all chalcone derivatives showed two doublets in the range of 7.99–7.92 ppm with coupling constant 16.12 Hz for two vinyl protons of s-cis double bond.

3.1. Photophysical properties

The spectral characteristics such as absorption (λ_{abs}), emission (λ_{em}), extinction coefficient (ε) and quantum yield (Φ) of the all new compounds (3a–3o and 6a–6e) were measured in methanol and results are presented in Table 4. In all compounds, structural modification occurs only at the terminal position of chalcones where aromatic rings with different substituents are attached. Such variations are expected to bring notable change in the absorption and emission spectra due to their differing electron releasing and electron donating abilities. The absorption spectra of compounds 3b, 3d, 3e, 3f, 3i, 3l and 3m showed two absorption bands in the range of 233–237 nm and 275–322 nm. Compound 3o showed one absorption band at 395 nm, whereas all other

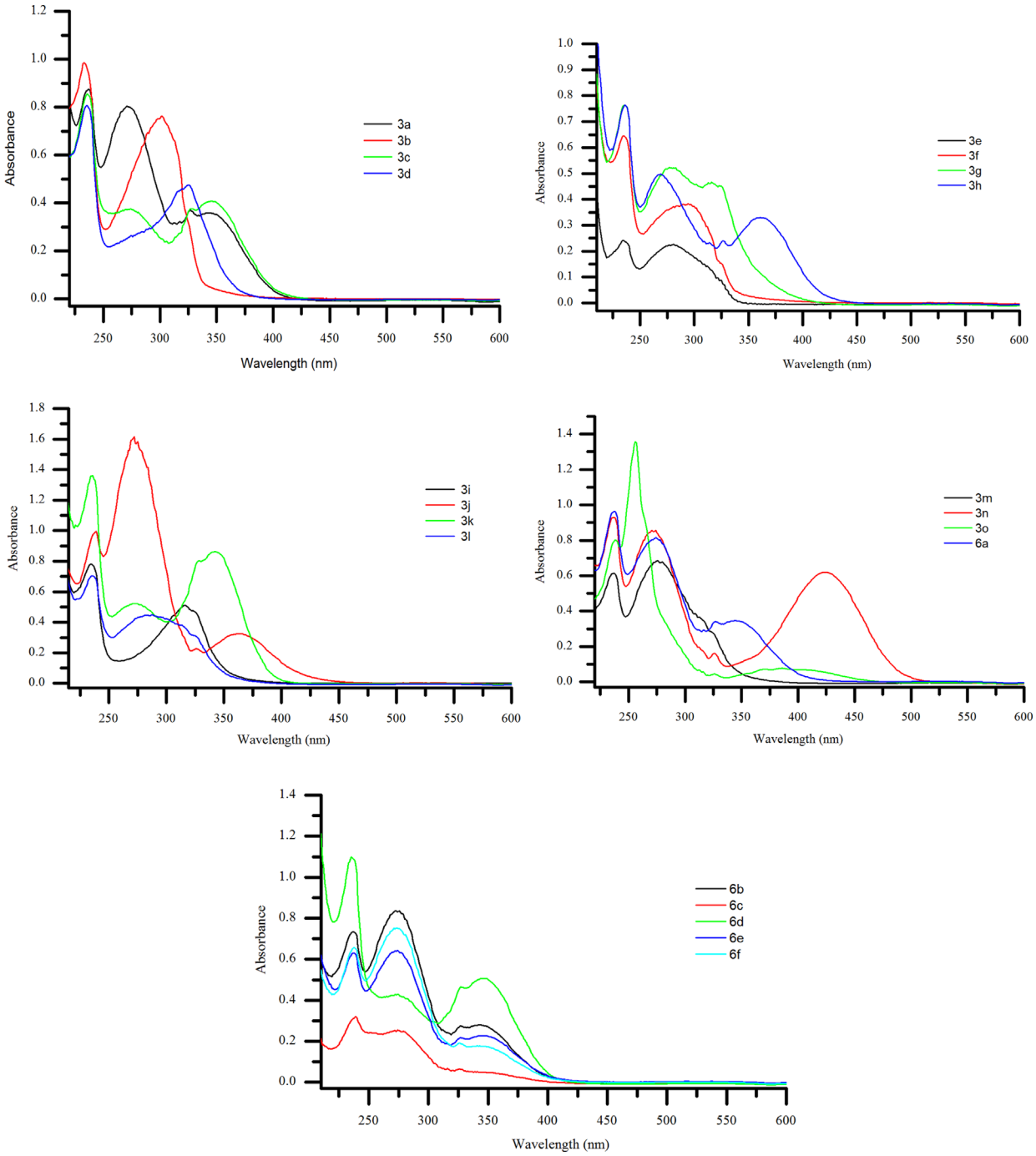


Fig. 2. Absorption spectra of all compounds (3a–3o, 6a–6e) in methanol (1×10^{-5} M).

compounds showed three absorption bands in the range of 234–239 nm, 269–279 nm and 319–423 nm as shown in Fig. 2 and listed in Table 4.

The broad absorption band at 319–423 nm may be attributed due to lower energy n–π^* transitions. Compound 3n with strong electron releasing dimethylamino group showed largest bathochromic shift with absorption maxima at 423 nm which may be due to intramolecular charge transfer from nitrogen atom of dimethylamino group to the acceptor carbonyl group. The emission spectra of all compounds are investigated and shown in Fig. 3.

Compounds having electron withdrawing substituents (3d, 3f, 3j) and halogen substituents (3c, 3g, 3i, 3l, 3m) over phenyl ring did not show emission in methanol. All other compounds (3a, 3b, 3e, 3h, 3k, 3n, 3o, 6a–6e) showed strong fluorescence in the range of 411–537 nm as shown in Fig. 3 with large stokes shift in range of 11,735–4526 cm^{-1} as listed in Table 4.

Compound 3b showed largest stoke shift of 11,735 cm^{-1} while compound 3o showed lowest stoke shift of 4526 cm^{-1}. The fluorescence quantum yields (Φ) were measured in methanol. Compound 3o with 9-anthryl ring at the terminal position of chalcone showed highest quantum yields (Φ) of 0.142, while compound 3b displaced lowest quantum yield (Φ) of 0.008.

We further investigated the influence of solvents on the photophysical properties of compound 3a. Absorption and emission spectra of 3a were measured in different solvents with varying polarities such as ethyl acetate, THF, methanol, hexane, DMF, DMSO, benzene, chloroform, acetonitrile, water and dioxane. The photophysical properties of 3a in various solvents are shown

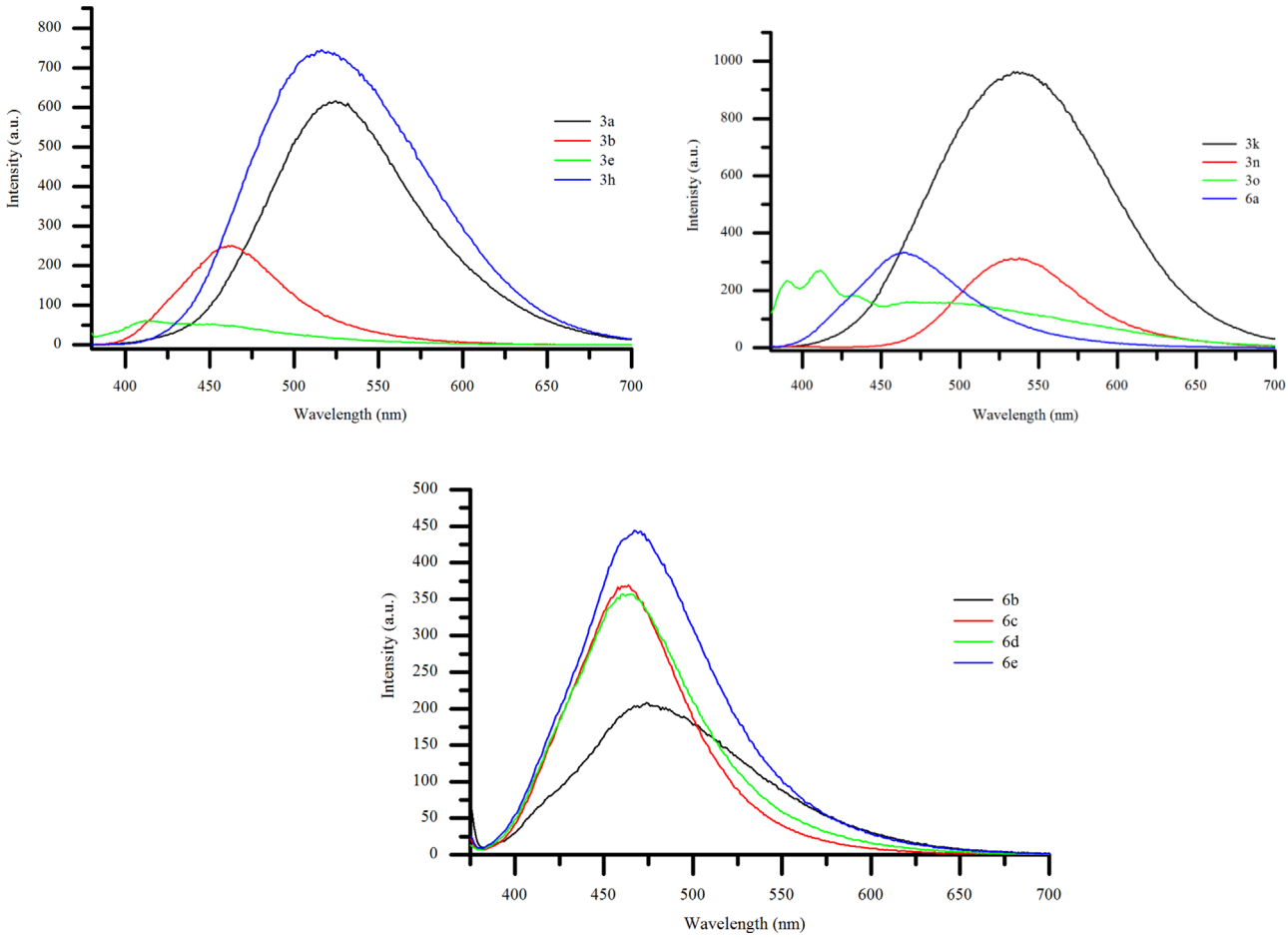


Fig. 3. Fluorescence spectra of compounds (3a, 3b, 3e, 3h, 3k, 3n, 3o, 6a–6e) in methanol.

Table 5
Absorption and fluorescence spectral data of compound 3a.

Solvent	ν_a (cm^{-1})	ν_f (cm^{-1})	$\nu_a-\nu_f$ (cm^{-1})	$\nu_a+\nu_f$ (cm^{-1})	$(\nu_a+\nu_f)/2$ (cm^{-1})	Quantum yield (Φ)
Ethylacetate	29,239	21,321	7918	50,560	25,280	0.033
THF	28,653	20,825	7828	49,478	24,739	0.044
Methanol	29,498	19,083	10,415	48,581	24,290.5	0.059
Hexane	28,985	22,522	6463	51,507	25,753.5	0.008
DMF	30,303	20,703	9600	51,006	25,503	0.032
DMSO	28,571	20,449	8122	49,020	24,510	0.058
Benzene	28,328	21,691	6637	50,019	25,009.5	0.032
Chloroform	26,954	20,964	5990	47,918	23,959	0.376
Acetonitrile	29,239	20,491	8748	49,730	24,865	0.022
Water	28,901	20,449	8452	49,350	24,675	0.085
Dioxane	29,325	20,920	5820	50,245	25,122.5	0.023

in Table 5. It can be inferred from Table 5 that compound 3a showed a bathochromically shifted emission maxima in polar solvents such as methanol, DMF, DMSO and water compared to non-polar solvents such as hexane and benzene. Quantum yield (Φ) of all compounds was measured in different solvents. Compound 3a showed highest quantum yield (0.376) in chloroform, and lowest quantum yield (0.008) in hexane which could be due to lower solubility of 3a in hexane.

The solvent–solute interactions of compound 3a with various solvents and their effect on emission spectra were further elaborated by multi-parameter correlation analysis as proposed by Kamlet–Taft [22] and Catalan [23]. Kamlet–Taft proposes the acidity (α), basicity (β) and polarizability (π^*) scale of solvents to determine the solvent–solute interactions as shown in Eq. (2), while Catalan proposes SPP^N, SA, SB scales to describe the polarizability, acidity and basicity of the solvents, respectively as

$$\upsilon_x = (\upsilon_x)_0 + C_\alpha\alpha + C_\beta\beta + C_{\pi*}\pi^* \quad (2)$$

$$\upsilon_x = (\upsilon_x)_0 + C_{SA}SA + C_{SB}SB + C_{SPP}SPP \quad (3)$$

Table 6
Adjusted coefficients for multiple linear regression analysis of fluorescence of compound 3a with the solvent polarity/polarizability, and acid base capacity using Kamlet–Taft and Catalan scales.

Kamlet–Taft	$(\upsilon_x)_0$ cm^{-1}	$C_{\pi*}$	C_α	C_β	R^2
ν_{flu}	21,512.45	−1581.16	161.81	−1589.73	0.89
Catalan	$(\upsilon_x)_0$ cm^{-1}	C^N_{SPP}	C_{SA}	C_{SB}	R^2
ν_{flu}	20,969.41	−2852.77	24.19	−3572.71	0.91

The correlation obtained for emission spectra of compound 3a using multi-linear regression analysis as proposed by Kamlet–Taft and Catalan is shown in Fig. S1 (see ESI†) and results are summarized in Table 6. Adjustments and correlation coefficients proposed by Kamlet–Taft and Catalan equations affecting the fluorescence band of 3a which describe the polarity/polarizability of the solvent ($C_{\pi*}$, SPP^N] are having a negative value, which corroborate the solvatochromic shifts with the solvent polarity. Negative values of C_β and C_{SB} indicate the bathochromic shift in emission with increase in electron donating ability of solvent, while small values of C_α or C_{SA} indicate that the electron accepting

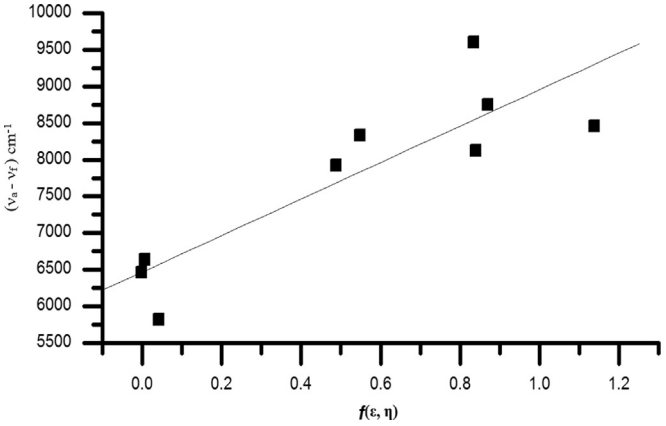


Fig. 4. Plot between $f(\varepsilon,\eta)$ *vs.* $(\nu_a-\nu_f)$ cm^{-1} for compound 3a.

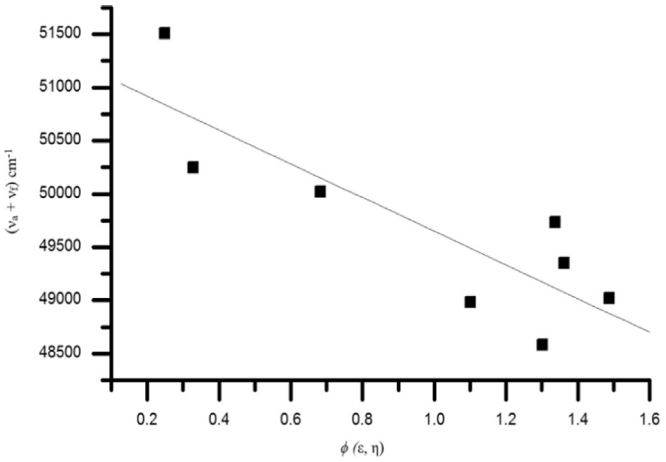


Fig. 5. Bilot–Kawski plot between $\varphi(\varepsilon,\eta)$ *vs.* $(\nu_a+\nu_f)$ cm^{-1} for compound 3a.

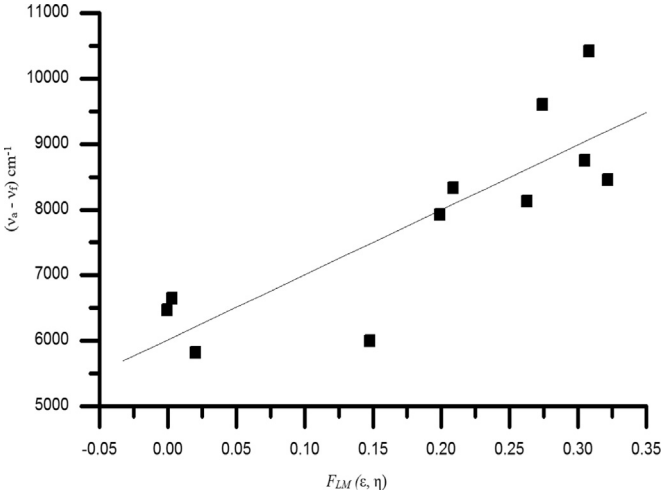


Fig. 6. Lippert–Mataga plot between $F_{LM}(\varepsilon,\eta)$ *vs.* $(\nu_a-\nu_f)$ cm^{-1} for compound 3a.

ability of solvents has a little effect on the emission spectra of compound 3a.

In view of importance of dipole moment determination of molecules in designing new optical materials, we have calculated the dipole moment of compound 3a using various solvatochromic methods. The ground state dipole moment of compound 3a was calculated using the Bilot–Kawski method [24] (Eq. (S8)) (see ESI†), while excited state dipole moment was estimated from

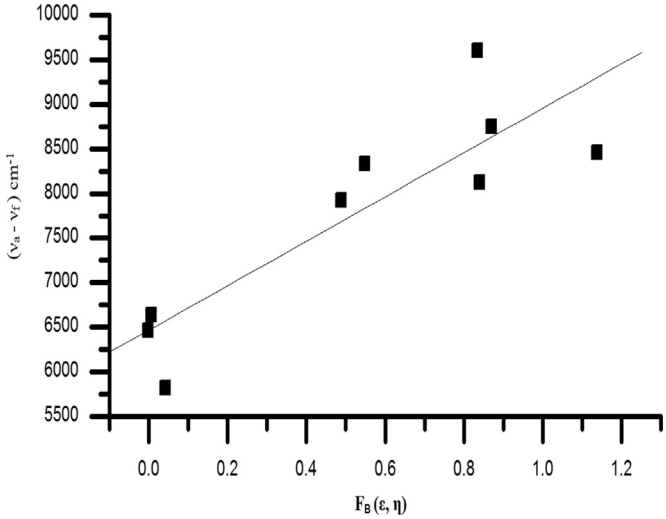


Fig. 7. Bakhshiev's plot between $FB(\varepsilon,\eta)$ *vs.* $(\nu_a-\nu_f)$ cm^{-1} for compound 3a.

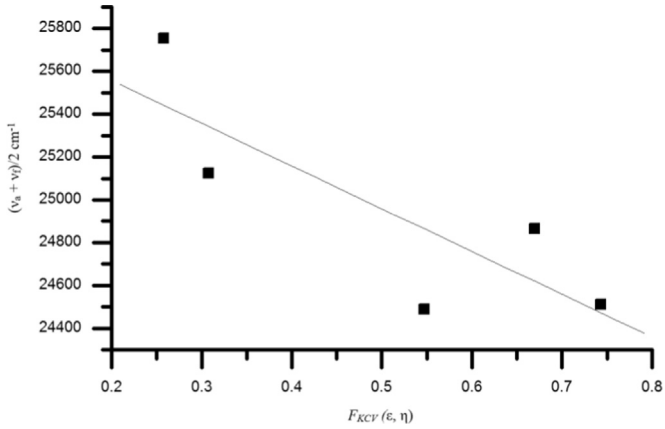


Fig. 8. Kawski–Chamma–Viallet plot between $FKCV(\varepsilon,\eta)$ *vs.* $(\nu_a+\nu_f)/2$ cm^{-1} for compound 3a.

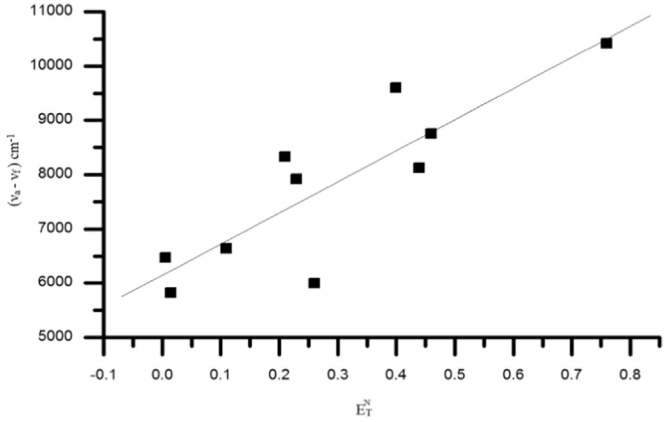


Fig. 9. Reichardts plot between E_T^N *vs.* $(\nu_a-\nu_f)$ cm^{-1} for compound 3a.

Bilot–Kawski, [24] Lippert–Mataga [25], Bakhshiev's [26], Kawski–Chamma–Viallet [27] and Reichardts methods [28]. Onsager cavity radius was obtained using Eq. (S7) (see ESI†). Various solvent polarity function values such as $f(\varepsilon,\eta)$, $\varphi(\varepsilon,\eta)$, $F_{LM}(\varepsilon,\eta)$, $F_B(\varepsilon,\eta)$, $F_{KCV}(\varepsilon,\eta)$ and E_T^N used in this work were taken from the literature [24–28] and are summarized in Table S1 (see ESI†). The

Table 7
Statistical parameters of various plots of compound 3a.

Plot	Slope (B)	Intercept	Number of data (n)	R
$\nu_a-\nu_f$ *vs.* $f(\varepsilon,\eta)$	2486.85	6469.75	10	0.86
Bilot–Kawski	−1583.25	51,233.0	8	0.84
Lippert–Mataga	9910.20	6015.10	11	0.85
Bakhshiev's	2486.85	6469.75	10	0.86
Kawski–Chamma–Viallet	−1998.25	25,957.40	5	0.86
Reichardts	5733.30	6146.21	10	0.85

Table 8
Ground and excited state dipole moment of compound 3a (in Debye D).

Onsager radius[a] (Å)	μ_g [b]	μ_e [c]	μ_e [d]	μ_e [e]	μ_e [f]	μ_e [g]	(μ_e/μ_g) [h]
5.261	1.081	4.882	13.050	7.075	6.380	6.012	4.516

$1D=3.33564\times10^{-30}$ C m. $=10^{-18}$ e.s.u.

[a] Calculated according to Eq. (S7).
[b] Ground state dipole moment calculated according to Bilot–Kawski Eq. (S8).
[c] Excited state dipole moment calculated according to Bilot–Kawski Eq. (S9).
[d] Excited state dipole moment calculated according to Lippert–Mataga Eq. (S12).
[e] Excited state dipole moment calculated according to Bakhshiev's Eq. (S15).
[f] Excited state dipole moment calculated according to Kawski–Chamma–Viallet Eq. (S18).
[g] Excited state dipole moment calculated according to Reichardts Eq. (S20).
[h] Calculated according to Eq. (S21).

excited state dipole moment was determined by solvatochromic methods. Therefore we plotted $f(\varepsilon,\eta)$ *vs.* $(\nu_a-\nu_f)$ (Fig. 4), Bilot–Kawski (Fig. 5), Lippert–Mataga (Fig. 6), Bakhshiev's (Fig. 7), Kawski–Chamma–Viallet (Fig. 8) and Reichardts (Fig. 9) plots by using Eqs. (S1), (S2), (S10), (S13), (S16) and (S19) (see ESI†), respectively. The statistical parameters obtained by these plots are summarized in Table 7. It can be seen from Table 7 that good correlation coefficient was obtained for each data plot.

Value of Onsager cavity radius, results of ground state and excited state dipole moment of 3a obtained by different solvatochromic methods are presented in Table 8. Ground state dipole moment (μ_g) was found to be 1.081 D as calculated by the Bilot–Kawski method. It can be seen from Table 8 that excited state dipole moment (4.882 D) is found to be higher than ground state dipole moment (1.081 D).

Excited state dipole moment (μ_e) ranged between 13.050 and 4.882 D as calculated by various methods. The difference in the ground state dipole moment and excited state dipole moment ($\Delta\mu$) as calculated by various methods comes in the range of 11.969–3.801 D. The large change in dipole moment ($\Delta\mu$) indicates that compound 3a is significantly more polar in its excited state than in its ground state and hence solvent–solute interactions are stronger in the excited state that tend to stabilize the excited electronic state. The higher excited state dipole moment also indicates a redistribution of charge densities between ground electronic state and excited states. We have observed a relatively good agreement between the excited state dipole moments observed from the Bilot–Kawski, Bakhshiev's, Kawski–Chamma–Viallet and Reichardts correlations. The excited state dipole moment obtained from the Lippert–Mataga method (13.050 D) is large compared to value obtained by other methods, as it does not consider polarizability effect of the solute. The change in dipole moment on excitation can be attributed to the change in the nature of emitting state and charge transfer.

Compound 3a and its precursor 2 were further subjected to thermogravimetric analysis in order to determine their thermal stability. Stepwise isothermal increase in temperature up to 900 °C at 10 °C/min was performed under nitrogen atmosphere and change in weight of the compound was measured as a function of temperature. Thermal stability is defined as the temperature at which approximately 95% of the composition of the compound remains stable. 96.3% of the weight composition of 3a was found to be stable up to temperature 261 °C and underwent thermal decomposition thereafter whereas the precursor 2 was found to be stable up to 173 °C.

4. Conclusion

In conclusion, we have synthesized a series of novel chloroquinoline based chalcones and their derivatives containing 1,2,3-triazole moiety. All new compounds were characterized by spectral data and single crystal X-ray crystallography. The absorbance and emission spectra of all compounds were investigated and it was observed that compounds having electron withdrawing or halogen substituents on phenyl ring did not show emission. The effect of various solvents over emission spectra of 3a was studied using Kamlet–Taft and Catalan polarity scales and it was infreed that it depends upon polarizability ($C_{\pi*}/C^{N}_{SPP}$) and electron donating ability (C_β/C_{SB}) parameters of solvent. The ground state and excited state dipole moments of compound 3a were determined using solvatochromic methods. The ground state dipole moment was estimated to be 1.081 D, while excited state dipole moment was calculated to be in the range of 11.969–3.801 D. Thermal stability of compound 3a and its precursor was also investigated using thermogravimetric analysis.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jlumin.2014.10.047.

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