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Synthesis of New Bicyclic Aziridines Containing Chalcone Analogs and Investigation of Their Photochromic Properties

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Ten new derivatives of 1,3-diazabicyclo[3.1.0]hex-3-enes linked *via* ether linkage to chalcones were synthesized and characterized by UV, FT-IR, ^{1}H NMR and ^{13}C NMR spectral techniques. The spectra of all synthesized compounds, confirmed structure-photochromic behavior relationships (SPBR) both in solution or in solid state by irradiation under UV light at 254 nm. In other efforts for first time photochromic behavior of ketoaziridines has been investigated.

Key Words : Bicyclic aziridine, Chalcone, Ketoaziridine, Photochromism

Introduction

Photochromic compounds have fascinated considerable interest because of their potential application in photonic and photoactive devices. Recently there has been significant scientific interest in the photochromic compounds use in optical memories, photo-switches, fluorescent switches, data-storage systems, fullcolor displays, molecular motors and mechanical machines, optical antenna, plastic banknotes, optoelectronic systems, metal-organic frameworks, polymeric micelles, wireless molecular-crystal actuators, liquid-crystalline actuators and responsive photonic crystals.[1-16]

Chalcones (1,3-diaryl-2-propene-1-ones) are the natural substances found in plants or prepared synthetically. They show many biological activities.[17] Photochemically, chalcone derivatives were reported to encompass excellent nonlinear optic property for optical communications and optical electronics, liquid crystal displays, and alignment film. Among various photocross-linkable groups, chalcones were also reported as photosensitive polymers, due to its excellent photoreactivity at UV absorption wavelength. Polymers that contain α,β-unsaturated carbonyl groups undergo cross-linking upon irradiation with UV light or an electron beam and are used as photoresists.[18-23]

Bicyclic aziridines (1,3-diazabicyclo[3.1.0]hex-3-enes) represent a very interesting class of organic compound, possessing exclusive photochromic properties and display good photochromic properties both in solid state and in solution. This compound form deeply colored, fairly stable materials under UV irradiation and the coloration-decoloration cycles of these compounds could be repeated over and over predominantly in solid state with less number of cycles in solution. These properties persuade us to consider the bicyclic aziridines as possible candidates in the search for radiochromic materials.[24-31]

Diverse systems are under study for information storage and optical switches. The majority of established systems show a positive photochromism. Positive photochromism defined as a phenomenon which shows bathochromic shift after UV irradiation at absorption band while negative photochromism defined as a phenomenon which shows hypsochromic shift after UV irradiation at absorption band. Inverse photochromism is encountered in spiropyran dyes and photoaddition of conjugated systems such as spiropyran dyes with cinnamoyl moiety, intramolecular [2π+2π] photocycloaddition cinnamate vinylogs. Polymers containing α,β-unsaturated carbonyl groups (cinnamoyl, chalcones, etc) undergo photocross-linking upon irradiation with UV light, known as negative-type photoresists.[32-39]

We herein report the synthesis of new bicyclic aziridines containing chalcones 19-28 (Fig. 1). The photochromic chalcones under UV irradiation indicate both positive and negative photochromism behaviors. In other efforts, for first time, photochromic behavior of ketoaziridines 17 and 18 has been investigated (Scheme 3).

Experimental

Materials and Measurements. Arylaldehydes, 4-hydroxyacetophenone, acetophenone are commerically available and were used as supplied. Ketoaziridines **17** and **18** were synthesized according to our previously reported procedures.[25] Solvents were dried by standard methods. The UV-Vis absorption spectra in the range of 200-800 nm (EtOH) as well as position of absorption band maxima for the initial (a) and photoinduced (b) photoisomers were measured with a Shimadzu UV-2100 spectrophotometer. Melting points were uncorrected and determined by Electrothermal 9100 melting point apparatus. Products were characterized by IR, ^{1}H NMR, ^{13}C NMR and mp, IR spectra were obtained on a Shimadzu IR-470 and FT-IR Bruker model VECTOR 22. All NMR data were recorded in $CDCl_3$ using Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in ppm (δ) using deuterated solvents as internal references.

Synthesis and Spectral Characterization of the Title Compounds.

Chalcones 6-10: Compounds **6-10** were prepared according to the reference.[46]

Preparation of the 1-Iodopropan-2-one 11: Chloroacetone (0.5 mL, 6 mmol) was added to a mixture of KI (1.16 g, 7 mmol), dry acetone (10 mL) and stirred at dark at rt for 5-6 h. The mixture was filtered and dried in vacuum leading to the formation of brown syrup (0.87 mmol, 90%). IR (KBr, cm^{-1}): 3500, 2950, 1700, 1415, 1360, 1220, 1130, 960.

Preparation of the Chalcone Derivative 12: Compound **6** (0.39 g, 2 mmol) was added to a mixture of K_2CO_3 (0.55 g, 4 mmol) and DMF (6 mL), then stirred for 10 min. To this was added gradually 1-iodopropan-2-one **11** (0.6 mL) dropwise over period of 5 min and the resulting mixture was stirred overnight at 25 °C. The reaction was monitored by TLC (EtOAc/petroleum ether 2:6). After completion of the reaction, H_2O (10 mL) was added. The precipitate was filtered off and dried at rt to yield **12** (0.476 g, 1.7 mmol, 85%) as a cream solid. mp 109-110 °C; IR (KBr, cm^{-1}): 3050-3100, 2950-2990, 1735, 1654, 1602, 1499, 1220, 824, 767, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 4.67 (s, 2H), 7 (d, J = 9.2 Hz, 2H), 7.44 (m, 3H), 7.55 (d, J = 15.6 Hz, 1H), 7.67 (dd, J = 6.4 Hz, J = 2.8 Hz, 2H), 7.83 (d, J = 15.6 Hz, 1H), 8.07 (d, J = 8.8 Hz, 2H).

Preparation of the Chalcone Derivative 13: Same procedure as compound **12** yielded compound **13**. (0.51 g, 1.64 mmol, 82%) as a yellow solid. mp 84-85 °C; IR (KBr, cm^{-1}): 3075, 3000, 2950, 2900, 2825, 1715, 1650, 1600, 1565, 1505, 1455, 1220, 1030, 820; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.88 (s, 3H), 4.66 (s, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 9.2 Hz, 2H), 7.44 (d, J = 15.6 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 15.2 Hz, 1H), 8.06 (d, J = 8.4 Hz, 2H).

Preparation of the Chalcone Derivative 14: Same procedure as compound **12** yielded compound **14**. (0.504 g, 1.6 mmol, 80%) as a cream solid. Yield 80%; mp 116-118 °C; IR (KBr, cm^{-1}): 3050, 2900, 1710, 1650, 1600, 1560, 1505, 1490, 1360, 1220, 1025, 810; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 4.67 (s, 2H), 6.99 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 15.6 Hz, 1H), 7.6 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 15.6 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H).

Preparation of the Chalcone Derivative 15: Same procedure as compound **12** yielded compound **15**. (0.481 g, 1.48 mmol, 74%) as a light brown solid. Yield 74%; mp 140-142 °C; IR (KBr, cm^{-1}): 3050, 3070, 2910, 1730, 1650, 1600, 1420, 1510, 1340, 1225, 1020, 825; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 4.69 (s, 2H), 7.02 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 15.6 Hz, 1H), 7.81 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 14.8 Hz, 1H), 8.09 (d, J = 8.8 Hz, 2H), 8.3 (d, J = 8.8 Hz, 2H).

Preparation of the Chalcone Derivative 16: Same procedure as compound **12** yielded compound **16**. (0.45 g, 1.52 mmol, 76%) as a yellow solid. Yield 76%; mp 72-74 °C; IR (KBr, cm^{-1}): 3240, 3050-3100, 2965, 1724, 1654, 1600, 1498, 1264, 1026, 868, 797; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 4.67 (s, 2H), 6.3 (br s, 1H, O-H), 6.94-6.99 (m, 3H), 7.19-7.32 (m, 3H), 7.51 (d, J = 15.6 Hz, 1H), 7.78 (d, J = 15.6 Hz, 1H), 8.05 (d, J = 8.8 Hz, 2H).

Preparation of the Title Compound 19: Ketoaziridine **17** (0.5 mmol), NH_4OAc (2.5 mmol), **12** (0.5 mmol) were dissolved in EtOH (2.5 mL) and stirred for 72 h at rt. The reaction was monitored by TLC (EtOAc/petroleum ether 3:6). After completion of the reaction, the mixture was cooled down for 20 min, filtered off, washed with small portions of hot EtOH and dried to yield **19** (0.225 g, 0.42 mmol, 85%) as a cream solid, which after irradiation with UV light converted to chromatic green-blue. mp 160-162 °C; IR (KBr, cm^{-1}): 3064, 2976, 2931, 1658, 1603, 1513, 1341, 1449, 1222, 1031, 829, 769, 696; (closed-form, 58%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_m$), 3.1 (d, J = 1.2 Hz, $1H_6$), 3.75 (d, J = 1.6 Hz, $1H_5$), 4.4 (d, J = 10.4 Hz, $1H_n$), 4.53 (d, J = 10 Hz, $1H_n$), 7.05 (t, J = 8.4 Hz, $2H_f$), 7.43-7.59 (m, $2H_d$, $1H_e$, $2H_h$, $2H_i$, $1H_j$, $1H_k$), 7.64-7.68 (m, $2H_b$), 7.81 (d, J = 15.6 Hz, $1H_l$), 7.95 (d, J = 7.2 Hz, $2H_c$), 8.03 (t, J = 9.6 Hz, $2H_g$), 8.2 (d, J = 8.8 Hz, $2H_a$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 43.2, 55.3, 71.2, 96.6, 114.6-135.1 (14 C_{Ar}), 144.2, 145.2, 147.4, 162.3, 169.9, 188.6; UV/Vis (EtOH): λ_{max} 204.5, 247.5, 312 nm; (open-form, 42%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_{m'}$), 2.73 (d, J = 1.6 Hz, $1H_{6'}$), 3.69 (d, J = 1.6 Hz, $1H_{5'}$), 4.33 (d, J = 9.6 Hz, $1H_{n'}$), 4.39 (d, J = 10 Hz, $1H_{n'}$), 7.05 (t, J = 8.4 Hz, $2H_{f'}$), 7.43-7.59 (m, $2H_{d'}$, $1H_{e'}$, $2H_{h'}$, $2H_{i'}$, $1H_{j'}$, $1H_{k'}$), 7.64-7.68 (m, $2H_{b'}$), 7.83 (d, J = 15.6 Hz, $1H_{l'}$), 7.89 (d, J = 7.2 Hz, $2H_{c'}$), 8.03 (t, J = 9.6 Hz, $2H_{g'}$), 8.23 (d, J = 8.8 Hz, $2H_{a'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 42.7, 57, 75, 96.9, 114.6-135.1 (14 C_{Ar}), 144.1, 145.3, 147.4, 162.9, 171.1, 188.7; UV/Vis (EtOH): λ_{max} 204.5, 224.5, 310.5, 405 nm.

Preparation of the Title Compound 20: Ketoaziridine **18** (0.5 mmol), NH_4OAc (2.5 mmol), **12** (0.5 mmol) were dissolved in EtOH (2 mL)/DMF (0.5 mL) and stirred for 4 days. The reaction was monitored by TLC (EtOAc/petroleum ether 3:6). After completion of the reaction, H_2O (5 mL) was added. The precipitate was filtered off and recrystallized from EtOH to yield **20** (0.196 g, 0.37 mmol, 74%) as a colorless solid, after irradiation with UV light the change of color was not observed. mp 94-96 °C; IR (KBr, cm^{-1}): 3063, 2968, 1656, 1602, 1526, 1344, 1448, 1219, 1029, 804, 769, 732, 692; (closed-form, 57%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (s, $3H_o$), 3.1 (d, J = 1.2 Hz, $1H_6$), 3.77 (d, J = 1.6 Hz, $1H_5$), 4.41 (d, J = 10.4 Hz, $1H_p$), 4.54 (d, J = 10 Hz, $1H_p$), 7.07 (t, J = 8.6 Hz, $2H_h$), 7.43-7.75 (m, $1H_c$, $1H_d$, $2H_f$, $1H_g$, $2H_j$, $2H_k$, $1H_l$, $1H_m$), 7.81 (d, J = 15.6 Hz, $1H_n$), 7.96 (d, J = 6.8 Hz, $2H_e$), 8.01 (d, J = 8.8 Hz, $2H_i$), 8.13 (d, J = 8 Hz, $1H_b$), 8.2 (s, $1H_a$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 43.1, 54.1, 71.2, 96.5, 114.7-135.1 (16 C_{Ar}), 140.1, 144.2, 148.4, 162.4, 169.1, 188.6; UV/Vis (EtOH): λ_{max} 208.5, 235, 320 nm; (open-form, 43%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (s, 3 $H_{o'}$), 2.75 (d, J = 1.6 Hz, $1H_{6'}$), 3.7 (d, J = 1.6 Hz, $1H_{5'}$), 4.34 (d, J = 9.6 Hz, $1H_{p'}$), 4.4 (d, J = 9.6 Hz, $1H_{p'}$), 7.07 (t, J = 8.6 Hz, $2H_{h'}$), 7.43-7.75 (m, $1H_{c'}$, $1H_{d'}$, $2H_{f'}$, $1H_{g'}$, $2H_{j'}$, $2H_{k'}$, $1H_{l'}$, $1H_{m'}$), 7.82 (d, J = 15.6 Hz, $1H_{n'}$), 7.9 (d, J = 7.2 Hz, $2H_{e'}$), 8.05 (d, J = 8.8 Hz, $2H_{i'}$), 8.17 (d, J = 8.8 Hz, $1H_{b'}$), 8.25 (s, $1H_{a'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 42.5, 56.7, 75, 96.9, 114.7-135.1 (16 C_{Ar}), 140.2, 144, 148.4,

162.9, 171.1, 188.8; UV/Vis (EtOH): λ_{max} 208.5, 225, 312.5, 384 nm.

Preparation of the Title Compound 21: Compound **21** was prepared by similar method to that used for compound **19**. Yield 80% (0.224 g, 0.4 mmol); mp 140-142 °C; as a colorless solid, which after irradiation with UV light converted to pistachio green; IR (KBr, cm^{-1}): 3065, 2932, 1654, 1598, 1512, 1343, 1453, 1219, 1028, 822, 743, 696; (closed-form, 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_l$), 3.1 (s, $1H_6$), 3.75 (s, $1H_5$), 3.88 (s, $3H_n$), 4.40 (d, J = 13.2 Hz, $1H_m$), 4.53 (d, J = 10 Hz, $1H_m$), 6.96 (d, J = 7.6 Hz, $2H_i$), 7.05 (t, J = 8.2 Hz, $2H_f$), 7.41 (d, J = 15.2 Hz, $1H_j$), 7.47-7.62 (m, $2H_b$, $2H_d$, $1H_e$, $2H_h$), 7.79 (d, J = 15.6 Hz, $1H_k$),7.95 (d, J = 6.8 Hz, $2H_c$), 8.02 (t, J = 9.2 Hz, $2H_g$), 8.23 (t, J = 8.8 Hz, $2H_a$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 43.2, 55.3, 55.4, 71.1, 96.6, 114.4-131.1 (12 C_{Ar}), 144.1, 145.2, 147.4, 161.6, 162.2, 169.9, 188.7; UV/Vis (EtOH): λ_{max} 207.5, 241.5, 304.5, 342.5 nm; (open-form, 37%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_{l'}$), 2.73 (s, $1H_{6'}$), 3.69 (s, $1H_{5'}$), 3.88 (s, $3H_{n'}$), 4.32 (d, J = 9.6 Hz, $1H_{m'}$), 4.40 (d, J = 13.2 Hz, $1H_{m'}$), 6.96 (d, J = 7.6 Hz, $2H_{i'}$), 7.05 (t, J = 8.2 Hz, $2H_f$), 7.41 (d, J = 15.2 Hz, $1H_{j'}$), 7.47-7.62 (m, $2H_{b'}$, $2H_{d'}$, $1H_{e'}$, $2H_{h'}$), 7.8 (d, J = 15.2 Hz, $1H_{k'}$), 7.89 (d, J = 7.2 Hz, $2H_{c'}$), 8.02 (t, J = 9.2 Hz, $2H_{g'}$), 8.23 (t, J = 8.8 Hz, $2H_{a'}$); ^{13}C NMR (400 MHz, $CDCl_3$) δ 27.5, 42.7, 55.4, 57, 75, 96.9, 114.4-131.1 (12 C_{Ar}), 143.9, 145.3, 147.4, 161.6, 162.7, 171.1, 188.8; UV/Vis (EtOH): λ_{max} 206.5, 247.5, 288, 341, 430 nm.

Preparation of the Title Compound 22: Compound **22** was prepared by similar method to that used for compound **20**. Yield 72% (0.201 g, 0.35 mmol); mp 96-98 °C; as a colorless solid, after irradiation with UV light the change of color was not observed; IR (KBr, cm^{-1}): 3064, 2964, 1654, 1597, 1519, 1346, 1450, 1221, 1028, 817, 733, 691; (closed-form, 64%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_n$), 3.1 (s, $1H_6$), 3.76 (s, $1H_5$), 3.88 (s, $3H_p$), 4.40 (d, J = 12.8 Hz, $1H_o$), 4.54 (d, J = 10.4 Hz, $1H_o$), 6.96 (d, J = 7.2 Hz, $2H_k$), 7.06 (t, J = 8.6 Hz, $2H_h$), 7.39-7.73 (m, $1H_c$, $1H_d$, $2H_f$, $1H_g$, $2H_j$, $1H_l$), 7.78 (d, J = 15.6 Hz, $1H_m$), 7.95 (d, J = 7.2 Hz, $2H_e$), 8 (d, J = 8.8 Hz, $2H_i$), 8.14 (d, J = 8.4 Hz, $1H_b$), 8.2 (s, $1H_a$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 43.1, 54.1, 55.4, 71.2, 96.5, 113.6-132.1 (14 C_{Ar}), 140.1, 144, 148.4, 161.6, 162.2, 169.1, 188.7; UV/Vis (EtOH): λ_{max} 207.5, 240, 345.5 nm; (open-form, 36%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_{n'}$), 2.75 (s, $1H_{6'}$), 3.69 (s, $1H_{5'}$), 3.88 (s, $3H_{p'}$), 4.33 (d, J = 9.6 Hz, $1H_{o'}$), 4.4 (d, J = 12.8 Hz, $1H_{o'}$), 6.96 (d, J = 7.2 Hz, $2H_{k'}$), 7.06 (t, J = 8.6 Hz, $2H_{h'}$), 7.39-7.73 (m, $1H_{c'}$, $1H_{d'}$, $2H_{f'}$, $1H_{g'}$, $2H_{j'}$, $1H_{l'}$), 7.8 (d, J = 15.2 Hz, $1H_{m'}$), 7.9 (d, J = 7.6 Hz, $2H_{e'}$), 8.04 (d, J = 8.8 Hz, $2H_{i'}$), 8.17 (d, J = 9.2 Hz, $1H_{b'}$), 8.25 (s, $1H_{a'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 42.5, 55.4, 56.7, 75, 96.9, 113.6-132.1 (14 C_{Ar}), 140.2, 143.9, 148.4, 161.6, 162.8, 171.1, 188.8; UV/Vis (EtOH): λ_{max} 205.5, 243.5, 288, 344, 405 nm.

Preparation of the Title Compound 23: Compound **23** was prepared by similar method to that used for compound **19**. Yield 76% (0.214 g, 0.38 mmol); mp 130-132 °C; as a yellow solid, which after irradiation with UV light converted to pale green; closed-form 100%: IR (KBr, cm^{-1}): 3068, 2931, 1663, 1602, 1514, 1342, 1451, 1223, 1024, 815, 742, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_l$), 3.09 (s, $1H_6$), 3.75 (s, $1H_5$), 4.4 (d, J = 10 Hz, $1H_m$), 4.53 (d, J = 10 Hz, $1H_m$), 7.04 (d, J = 8.4 Hz, $2H_f$), 7.4-7.6 (m, $2H_b$, $2H_d$, $1H_e$, $2H_h$, $2H_i$, $1H_j$), 7.76 (d, J = 15.6 Hz, $1H_k$), 7.94 (d, J = 7.2 Hz, $2H_c$), 8.01 (d, J = 8.4 Hz, $2H_g$), 8.2 (d, J = 8.4 Hz, $2H_a$); UV/Vis (EtOH): λ_{max} 206, 233, 319 nm; (open-form, with UV irradiation): UV/Vis (EtOH): λ_{max} 206.5, 228, 317.5, 408 nm.

Preparation of the Title Compound 24: Compound **24** was prepared by similar method to that used for compound **20**. Yield 68% (0.192 g, 0.34 mmol); mp 90-92 °C; as a colorless solid, after irradiation with UV light the change of color was not observed; IR (KBr, cm^{-1}): 3066, 2964, 1657, 1602, 1527, 1346, 1447, 1221, 1025, 809, 693; (closed-form, 59%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_n$), 3.09 (s, $1H_6$), 3.76 (s, $1H_5$), 4.41 (d, J = 10.8 Hz, $1H_o$), 4.54 (d, J = 10 Hz, $1H_o$), 7.07 (t, J = 9.2 Hz, $2H_h$), 7.4-7.79 (m, $1H_c$, $1H_d$, $2H_f$, $1H_g$, $1H_l$, $1H_m$, $2H_j$, $2H_k$), 7.95 (d, J = 7.2 Hz, $2H_e$), 8.0 (d, J = 8.8 Hz, $2H_i$), 8.14 (d, J = 8 Hz, $1H_b$), 8.2 (s, $1H_a$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 43.1, 54.1, 71.2, 96.5, 114.7-136.3 (14 C_{Ar}), 140.1, 142.7, 148.4, 162.5, 170, 188.3; UV/Vis (EtOH): λ_{max} 208, 238.5, 324 nm; (open-form, 41%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_{n'}$), 2.75 (s, $1H_{6'}$), 3.68 (s, $1H_{5'}$), 4.34 (d, J = 9.6 Hz, $1H_{o'}$), 4.41 (d, J = 10.8 Hz, $1H_{o'}$), 7.07 (t, J = 9.2 Hz, $2H_{h'}$), 7.4-7.79 (m, $1H_{c'}$, $1H_{d'}$, $2H_{f'}$, $1H_{g'}$, $1H_{l'}$, $1H_{m'}$, $2H_{j'}$, $2H_{k'}$), 7.9 (d, J = 7.6 Hz, $2H_{e'}$), 8.04 (d, J = 8.8 Hz, $2H_{i'}$), 8.18 (d, J = 8 Hz, $1H_{b'}$), 8.24 (s, $1H_{a'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 42.5, 56.7, 75, 96.9, 114.7-136.3 (14 C_{Ar}), 140.2, 142.5, 148.4, 163, 171.1, 188.3; UV/Vis (EtOH): λ_{max} 207, 231, 281, 321, 390 nm.

Preparation of the Title Compound 25: Compound **25** was prepared by similar method to that used for compound **19**. Yield 65% (0.187 g, 0.32 mmol); mp 214-216 °C; as a khaki solid, which after irradiation with UV light converted to russet color; IR (KBr, cm^{-1}): 3070, 2965, 1663, 1601, 1516, 1343, 1420, 1227, 1025, 829, 697; (closed-form, 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_l$), 3.08 (s, $1H_6$), 3.76 (s, $1H_5$), 4.42 (d, J = 10 Hz, $1H_m$), 4.49 (d, J = 18.4 Hz, $1H_m$), 7.07 (t, J = 8.6 Hz, $2H_f$), 7.39-7.83 (m, $2H_c$, $2H_d$, $1H_e$, $2H_b$, $1H_j$, $1H_k$), 7.89-8.06 (m, $2H_h$, $2H_g$), 8.18-8.30 (m, $2H_a$, $2H_i$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 43.3, 55.3, 71.2, 96.5, 114.6-141.3 (14 C_{Ar}), 145.2, 147.4, 148.5, 162.8, 170.1, 187.7; UV/Vis (EtOH): λ_{max} 207, 255, 307 nm; (open-form, 35%): ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.74 (s, $3H_{l'}$), 2.74 (s, $1H_{6'}$), 3.74 (s, $1H_{5'}$), 4.32-4.41 (m, $2H_{m'}$), 7.05-7.09 (t, J = 8.6 Hz, $2H_{f'}$), 7.39-7.83 (m, $2H_{c'}$, $2H_{d'}$, $1H_{e'}$, $2H_{b'}$, $1H_{j'}$, $1H_{k'}$), 7.89-8.06 (m, $2H_{h'}$, $2H_{g'}$), 8.18-8.30 (m, $2H_{a'}$, $2H_{i'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7, 42.7, 56.1, 75, 96.8, 114.6-141.3 (14 C_{Ar}), 145.2, 147.4, 148.5, 162.8, 170.1, 187.8; UV/Vis (EtOH): λ_{max} 207.5, 271, 410 nm.

Preparation of the Title Compound 26: Compound **26** was prepared by similar method to that used for compound **20**. Yield 61% (0.176 g, 0.3 mmol); mp 123-125 °C; as a colorless solid, after irradiation with UV light the change of

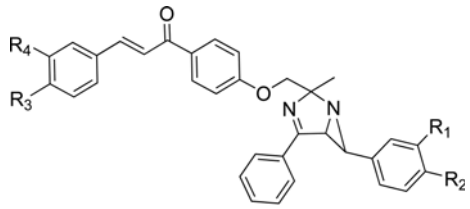
color was not observed; IR (KBr, cm^{-1}): 3069, 2931, 1664, 1601, 1522, 1345, 1448, 1223, 1026, 828, 769, 732, 693; (closed-form, 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (s, $3H_n$), 3.09 (s, $1H_6$), 3.77 (d, J = 1.6 Hz, $1H_5$), 4.42 (d, J = 8.8 Hz, $1H_o$), 4.55 (d, J = 10.4 Hz, $1H_o$), 7.08 (d, J = 8.8 Hz, $2H_h$), 7.43-7.85 (m, 9H, $1H_c$, $1H_d$, $2H_e$, $2H_f$, $1H_g$, $1H_l$, $1H_m$), 7.95 (d, J = 7.2 Hz, $2H_j$), 8.02 (d, J = 9.2 Hz, $2H_i$), 8.13-8.19 (m, $1H_b$), 8.19 (s, $1H_a$), 8.23-8.31 (m, $2H_k$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 43.1, 54.1, 71.2, 96.4, 114.9-148.4 (17 C_{Ar}), 162.8, 170, 187; UV/Vis (EtOH): λ_{max} 207.5, 253.5, 326.5 nm (open-form, 35%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (s, $3H_{n'}$), 2.76 (s, $1H_{6'}$), 3.68 (d, J = 1.2 Hz, $1H_{5'}$), 4.34-4.43 (m, $2H_{o'}$), 7.11 (d, J = 9.2 Hz, $2H_{h'}$), 7.43-7.85 (m, 9H, $1H_{c'}$, $1H_{d'}$, $2H_{e'}$, $2H_{f'}$, $1H_{g'}$, $1H_{l'}$, $1H_{m'}$), 7.9 (d, J = 7.2 Hz, $2H_{j'}$), 8.06 (d, J = 8.8 Hz, $2H_{i'}$), 8.13-8.19 (m, $1H_{b'}$), 8.23 (s, $1H_{a'}$), 8.23-8.31 (m, $2H_{k'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 42.5, 57, 74.1, 96.8, 114.9-148.4 (17 C_{Ar}), 162.8, 170, 187; UV/Vis (EtOH): λ_{max} 208, 251, 328, 383 nm.

Preparation of the Title Compound 27: Compound **27** was prepared by similar method to that used for compound **19**. Yield 81% (0.221 g, 0.4 mmol); mp 116-118 °C; as a yellow solid, which after irradiation with UV light converted to green; IR (KBr, cm^{-1}): 3250, 3066, 2934, 1659, 1600, 1516, 1344, 1449, 1254, 1029, 830, 784, 742, 695; (closed-form, 51%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_n$), 3.19 (s, $1H_6$), 3.78 (s, $1H_5$), 4.5 (d, J = 10 Hz, $1H_o$), 4.41 (d, J = 10 Hz, $1H_o$), 6.92-6.99 (m, $2H_f$, $1H_i$), 7.08 (br s, $1H_p$), 7.15-7.29 (m, $1H_h$, $1H_k$), 7.39 (d, J = 16 Hz, $1H_l$), 7.45-7.58 (m, $2H_b$, $2H_d$, $1H_e$, $1H_j$), 7.63 (d, J = 16.4 Hz, $1H_m$), 7.9-8.02 (m, $2H_c$, $2H_g$), 8.20 (d, J = 8.4 Hz, $2H_a$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 43.3, 55.2, 70.1, 96.4, 114.5-136.5 (14 C_{Ar}), 144.1, 145.1, 147.4, 156.6, 162.2, 170.4, 188.7; UV/Vis (EtOH): λ_{max} 205.5, 250, 304 nm; (open-form, 49%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, $3H_{n'}$), 2.76 (s, $1H_{6'}$), 3.76 (s, $1H_{5'}$), 4.36 (d, J = 9.6 Hz, $1H_{o'}$), 4.31 (d, J = 9.6 Hz, $1H_{o'}$), 6.92-6.99 (m, $2H_{f'}$, $1H_{i'}$), 7.08 (br s, $1H_{p'}$), 7.15-7.29 (m, $1H_{h'}$, $1H_{k'}$), 7.39 (d, J = 16 Hz, $1H_{l'}$), 7.45-7.58 (m, $2H_{b'}$, $2H_{d'}$, $1H_{e'}$, $1H_{j'}$), 7.63 (d, J = 16.4 Hz, $1H_{m'}$), 7.9-8.02 (m, $2H_{c'}$, $2H_{g'}$), 8.23 (d, J = 8.4 Hz, $2H_{a'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 42.7, 57, 74.8, 96.8, 114.5-136.5 (14 C_{Ar}), 143.1, 145.1, 147.5, 156.6, 162.8, 171.5, 188.8; UV/Vis (EtOH): λ_{max} 206, 254, 300, 402.5 nm.

Preparation of the Title Compound 28: Compound **28** was prepared by similar method to that used for compound **20**. Yield 75% (0.205 g, 0.37 mmol); mp 110-112 °C; as a colorless solid, after irradiation with UV light the change of color was not observed; IR (KBr, cm^{-1}): 3250, 3065, 2931, 1660, 1600, 1525, 1347, 1449, 1252, 1030, 827, 782, 733, 688; (closed-form, 57%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (s, $3H_p$), 3.18 (s, $1H_6$), 3.79 (s, $1H_5$), 4.42 (d, J = 10.4 Hz, $1H_q$), 4.51 (d, J = 10.4 Hz, $1H_q$), 6.91 (d, J = 7.6 Hz, $1H_k$), 6.98 (d, J = 8.8 Hz, $2H_h$), 7.1 (br s, $1H_r$), 7.15-7.29 (m, $1H_j$, $1H_m$), 7.39 (d, J = 15.6 Hz, $1H_n$), 7.45-7.75 (m, $1H_d$, $2H_f$, $1H_g$, $1H_l$, $1H_o$, $1H_c$), 7.9-8.05 (m, $2H_i$, $2H_e$), 8.13-8.21 (m, $1H_b$), 8.21 (s, $1H_a$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 43.1, 54.9, 74.8, 96.4, 114.6-139.1 (15 C_{Ar}), 139.1, 144.1, 148.4, 156.6, 162.3, 170.4, 188; UV/Vis (EtOH): λ_{max} 206.5, 245, 318 nm; (open-form, 43%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (s, $3H_{p'}$), 2.77 (s, $1H_{6'}$), 3.72 (s, $1H_{5'}$), 4.33 (d, J = 10.4 Hz, $1H_{q'}$), 4.40 (d, J = 10 Hz, $1H_{q'}$), 6.91 (d, J = 7.6 Hz, $1H_{k'}$), 7.03 (d, J = 8.8 Hz, $2H_{h'}$), 7.1 (br s, $1H_{r'}$), 7.15-7.29 (m, $1H_{j'}$, $1H_{m'}$), 7.39 (d, J = 15.6 Hz, $1H_{n'}$), 7.45-7.75 (m, $1H_{d'}$, $2H_{f'}$, $1H_{g'}$, $1H_{l'}$, $1H_{o'}$, $1H_{c'}$), 7.9-8.05 (m, $2H_{i'}$, $2H_{e'}$), 8.13-8.21 (m, $1H_{b'}$), 8.24 (s, $1H_{a'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 42.5, 57, 71, 96.8, 114.6-139.1 (15 C_{Ar}), 140, 144.1, 148.4, 156.6, 162.8, 170.4, 188; UV/Vis (EtOH): λ_{max} 207.5, 249, 312.5, 385 nm.

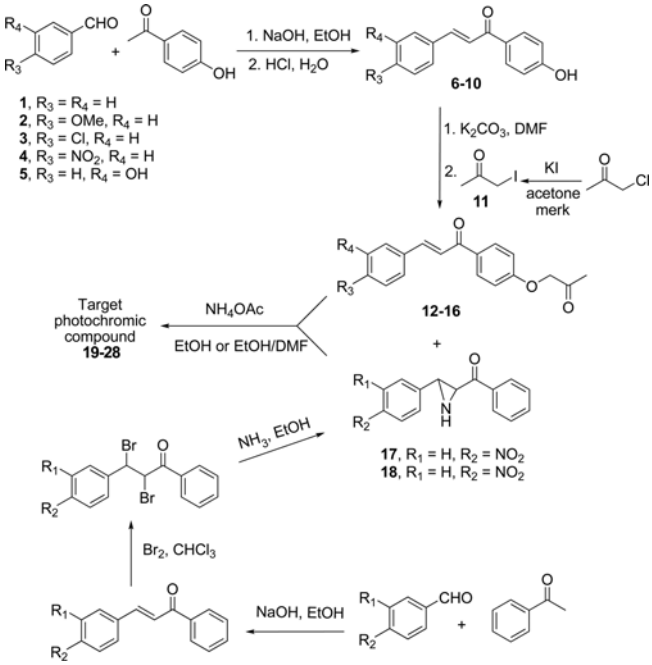
Results and Discussion

Photochromic compounds **19-28** prepared from one-pot MCRs (multicomponents reactions) of hydroxy chalcones **12-16**, ketoaziridines **17-18** and excess NH_4OAc. Structure of photochromic bicyclic aziridines are shown in Figure 1.

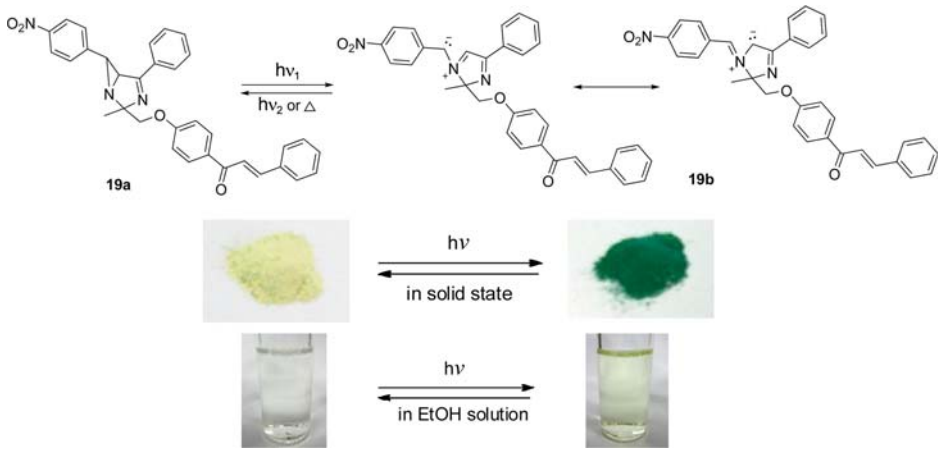


19, R_1 = H, R_2 = NO_2, R_3 = H, R_4 = H
20, R_1 = NO_2, R_2 = H, R_3 = H, R_4 = H
21, R_1 = H, R_2 = NO_2, R_3 = OMe, R_4 = H
22, R_1 = NO_2, R_2 = H, R_3 = OMe, R_4 = H
23, R_1 = H, R_2 = NO_2, R_3 = Cl, R_4 = H
24, R_1 = NO_2, R_2 = H, R_3 = Cl, R_4 = H
25, R_1 = H, R_2 = NO_2, R_3 = NO_2, R_4 = H
26, R_1 = NO_2, R_2 = H, R_3 = NO_2, R_4 = H
27, R_1 = H, R_2 = NO_2, R_3 = H, R_4 = OH
28, R_1 = NO_2, R_2 = H, R_3 = H, R_4 = OH

Figure 1. Structure of photochromic bicyclic aziridines.



Scheme 1. Synthetic route for preparation of photochromic compounds **19-28**.



Scheme 2. Photochromic reaction in the solution and solid states.

First, a series of hydroxy chalcone derivatives **6-10** was prepared *via* Claisen-Schmidt condensation of **1-5** benzaldehydes and 4-hydroxy acetophenone by route depicted in Scheme 1. Then, the reaction of these premade hydroxy chalcones **6-10** with freshly prepared iodoacetone in the presence of K_2CO_3 in DMF lead to the formation of chalcones with keto ether link. The structure of these chalcones was characterized by IR and ^{1}H NMR spectra. In other efforts counterparts ketoaziridines **17** and **18** were synthesized according to our previously described method (Scheme 1).[24,25]

Photochromic compounds **19-28** were prepared in good yields *via* one-pot click reaction of one equivalent of premade chalcones, one equivalent of premade ketoaziridines, and 5 equivalents of ammonium acetate under anhydrous condition (Scheme 1). The structure of products was characterized by IR, ^{1}H NMR, ^{13}C NMR and UV spectra.

These photochromic compounds showed good photochromic properties both in solution and in solid state, and could switch between their colorless closed-ring photoisomers and colored open-ring photoisomers, *e.g.* compound **19a** (Scheme 2).

The structures of both closed-ring and open-ring photoisomers were characterized and confirmed by UV, FT-IR, ^{1}H NMR and ^{13}C NMR spectral techniques. ^{1}H NMR of **19** in upfield showed two signals for C5 and C6 protons and signals of dd for diastereotopic methylene protons n. Transformation for each isomer is best ascertained by comparing the total integral of characteristic signals C5, C6 and n with C5', C6' and n'. ^{1}H NMR of compound **19** is shown in Figure 2 and the signals related to the two photoisomers are characterized. The equilibrium ratio for each photoisomer at steady state was easily assigned based on the analysis of the integration of some characteristic signals. Only compound **23** showed closed-ring phtoisomer completely. ^{13}C NMR of all compounds, except **23**, indicates both photoisomers. IR, ^{1}H NMR and ^{13}C NMR spectra display the expected signals (See Supplementary Material). Equilibrium ratio for photoisomers, yield and mp of photochromic compounds are summarized in Table 1.

The photochromic reactivity of bicyclic aziridines **19-28**

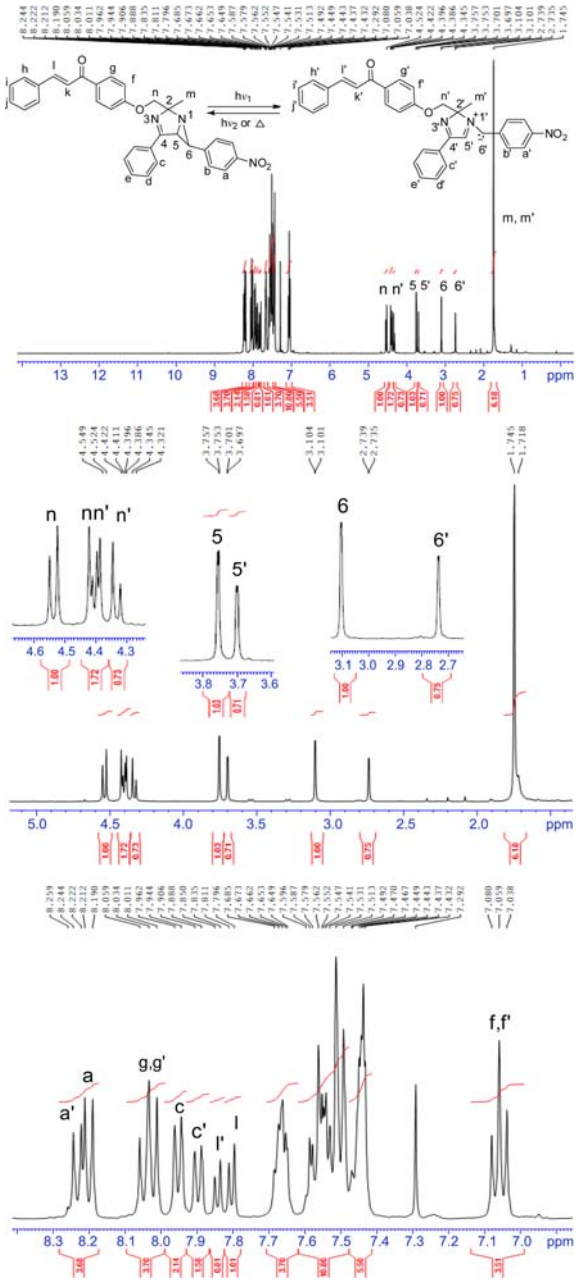


Figure 2. ^{1}H NMR of photochromic compound **19**.

Table 1. Equilibrium ratio for photoisomers, yield and melting point of photochromic compounds **19-28**

Entry	Compound	Equilibrium ratio C:O isomer[a]	Melting point (°C)	Yield (%)
1	**19**	58:42	160-162	85
2	**20**	57:43	94-96	74
3	**21**	63:37	140-142	80
4	**22**	64:36	96-98	72
5	**23**	100:0	130-132	76
6	**24**	59:41	90-92	68
7	**25**	65:35	214-216	65
8	**26**	65:35	123-125	61
9	**27**	51:49	116-118	81
10	**28**	57:43	110-112	75

[a]C:O (Close-ring photoisomer: Open-ring photoisomer).

was examined in EtOH solution. Their absorption spectra changed by UV light at RT (1.0×10^{-4} mol/L) (See Supplementary Material). Compounds **19-28** exhibited good photochromic properties and can transform between their colorless closed-ring photoisomers (**19a-28a**) and colored open-ring photoisomers (**19b-28b**) by alternating irradiation with UV light, as monitored using UV-vis absorption spectroscopy. In general, the absorption of the ring-closed photoisomer of compounds **19-28** appear at shorter wavelength, while the absorption of the ring-open photoisomers take place at a longer wavelength. Upon irradiation with 254 nm light, absorption bands appear in visible region and solutions turn pale green as a result of the cycloreversion reactions which produce **19b-28b**. The coloration-decoloration cycles of these compounds can repeat over and over. Among **19-28** only derivatives of *para*-nitro ketoaziridine **17** undergo reversible photochromic reactions in a crystalline state. By increasing the duration of irradiation or exposure to sun light the intensity of colour enhances, due to the increase of population of open form in the crystal forms. In this condition the cream solid **19** changes to chromatic green-blue solid, while solids **21**, **23**, **25**, **27** with white, yellow, khaki, yellow colors change to pistachio green, pale green, russet, green solids, respectively. (See the Change of Color in Supplementary Material).

Figures 3 and 4 show the change of absorption spectra of

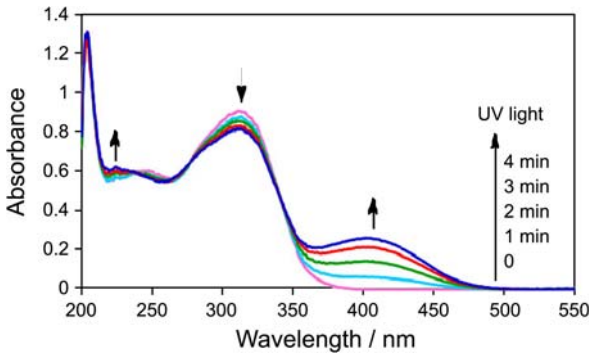


Figure 3. Absorption spectral changes of bicyclic aziridine **19** in EtOH solution at rt (1.0×10^{-4} mol/L) with UV light irradiation.

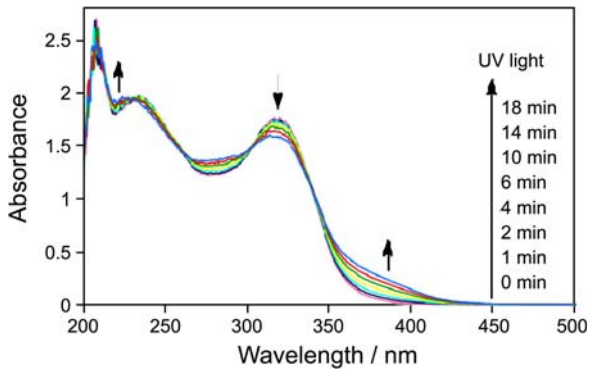


Figure 4. Absorption spectral changes of bicyclic aziridine **20** in EtOH solution at rt (1.0×10^{-4} mol/L) with UV light irradiation.

bicyclic aziridines **19** and **20** in EtOH solution. The colorless solution of **19a** changes to a green solution. Compound **19** exhibits absorptions maxima at 247.5 and 312 nm at 0 s (ring-closed photoisomer), UV irradiation causes absorption at 405 nm for **19b** due to the formation of zwitterionic double charged imine ylide (ring-open photoisomer). Compound **20** exhibits absorptions maxima at 235 and 320 at 0 s (ring-closed photoisomer), an increase of intensity at 384 nm is due to the formation of **20b** (open form photoisomer).

The negative photochromism is attributed to the formation of [2π+2π] cyclobutane ring of C=C bond of chalcone. This phenomenon upon irradiation with UV light was demonstrated from a decrease in the absorbance bands at 312 and 320 nm and simultanously increase the absorbance bands at

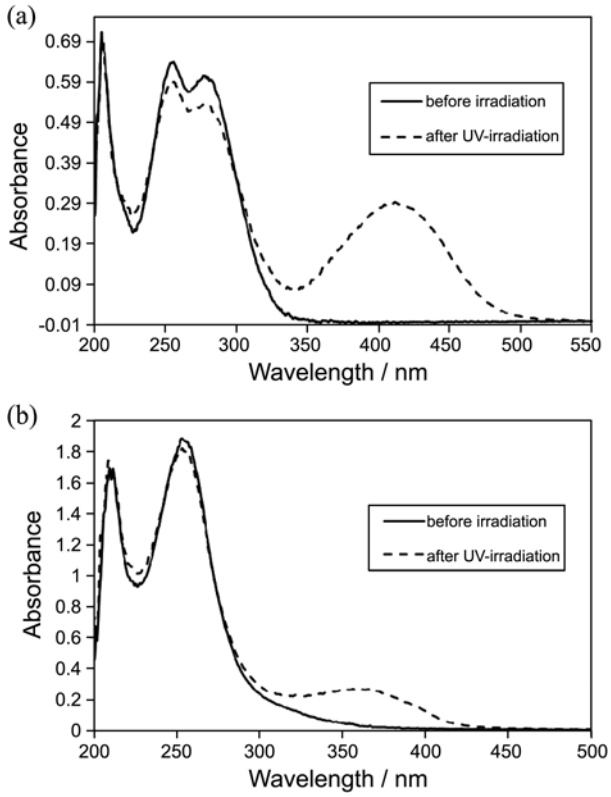


Figure 5. UV-Vis spectra of compounds **17** and **18**, before (solid line) and after 5 min UV irradiation (dashed): (a) **17**, (b) **18**.

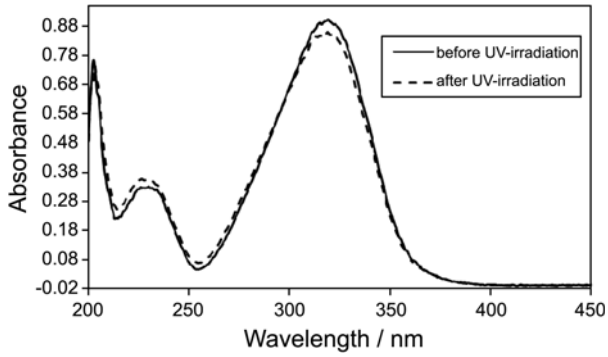
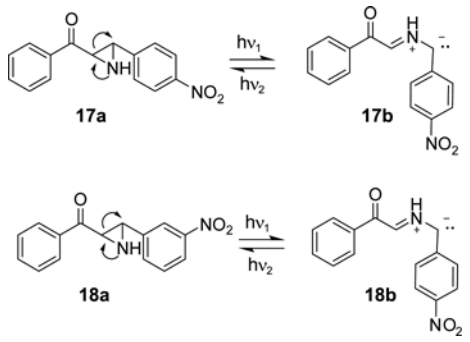
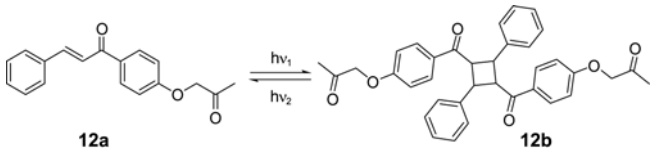


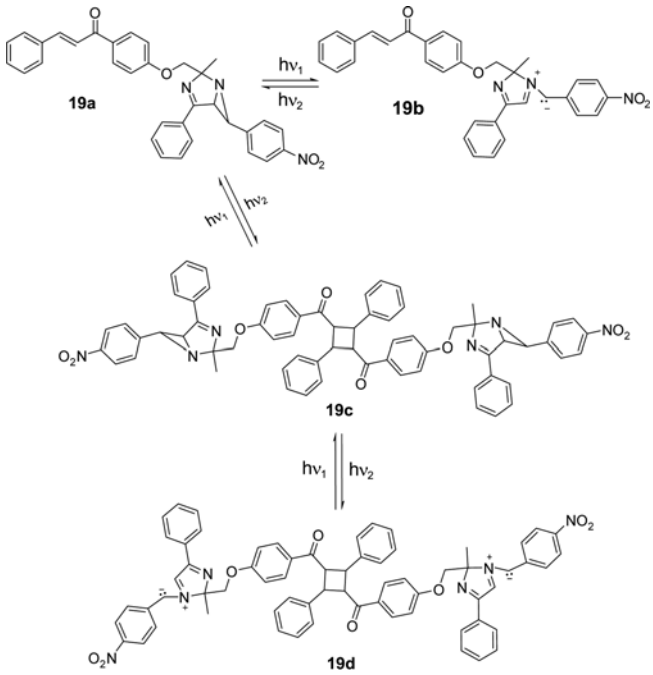
Figure 6. UV-Vis spectrum of **12a** before (solid line) and after 5 min UV irradiation **12b** (dashed).



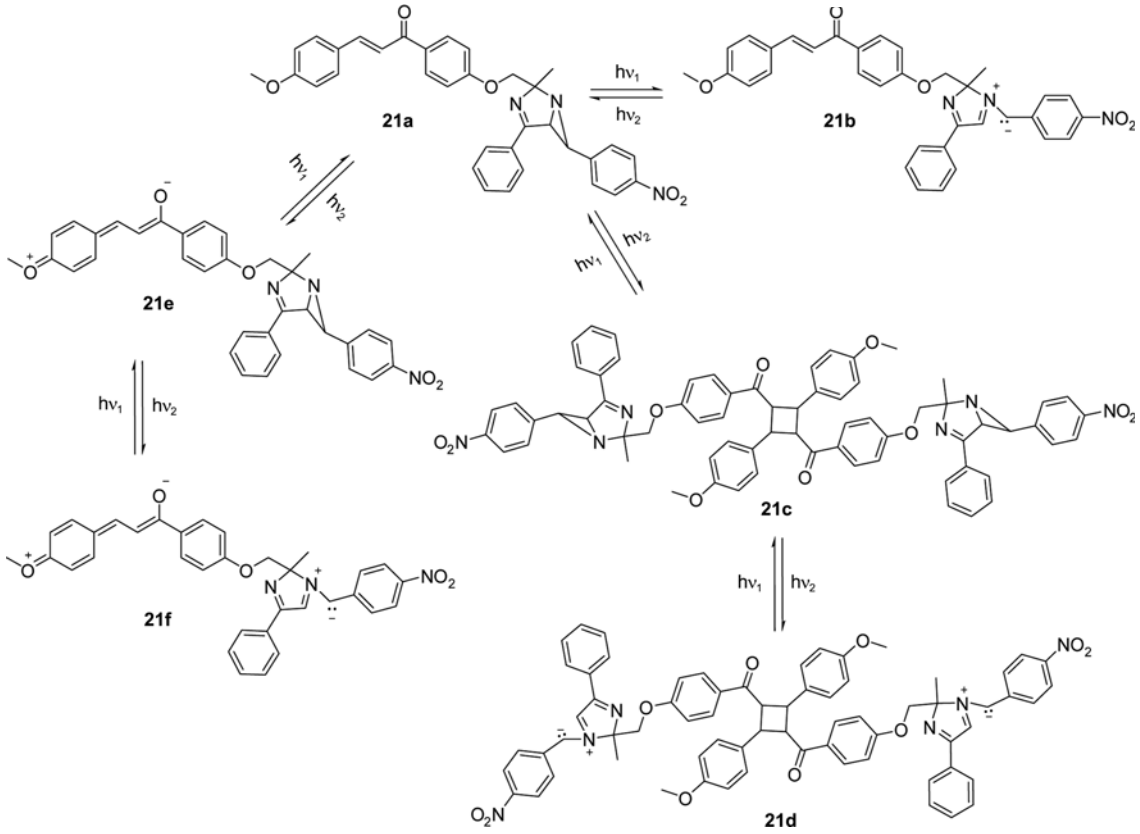
Scheme 3. Mechanism of photochromic process of ketoaziridines **17** and **18**.



Scheme 4. Mechanism of photochemical reaction of chalcone **12**.



Scheme 5. Mechanism of photochromic reaction of **19a**: positive photochromism and negative photochromism.



Scheme 6. Photochromic reaction of chalcone contains methoxy groups **21**.

230 nm region and shift the absorption bands at 247.5 and 235 nm to lower wavelengths 224 and 225 nm, respectively. However, for compound **20** with nitro group at the *meta* position in solid state the change of color was not observed.

The UV-Vis spectra of ketoaziridines **17** and **18** recorded in EtOH solution showed photochromic behavior (Figure 5).

New absorption bands for **17** and **18** upon irradiation with UV, were immerged at 411.5 and 366 nm, respectively. This phenomenon is due to the ring-opening of aziridine ring (Scheme 3). Figure 6 shows the absorption spectra of chalcone **12**. A decrease in the intensity at 319 nm band, and an increase in 230 nm band and shift this band to 226.5 nm upon 5 min UV irradiation attributed to the [2π+2π] cyclization reaction (Scheme 4).[2,19,32,37-43]

By comparison of UV spectra it can be understood that compounds **12**, **17** and **18** and photochromic compounds **19** and **20** upon UV irradiation goes under two photochromic processes: 1) aziridine ring opening that cause a shift to higher wavelength **19b** (positive photochromism); 2) photochemical [2π+2π] superficial ring closure cyclization of chalcone that shift the absorption band to lower wavelength **19d** *via* **19c** (negative photochromism) (Scheme 5).

Due to the electron releasing ability of methoxy group in *para* position of chalcone moiety another probable mechanism is still achievable. According to this mechanism *s-cis* chalcone **21a** changes to *s-trans* chalcone **21e** upon irradiation with UV light (Scheme 6). *E-Z* photoisomerization is very interesting in the application of photo-alignment of liquid crystal device applications and insulated molecular wires.[44,45]

This phenomenon is confirmed by the infrared spectral analysis in terms of the change and shift of the C=O absorption band at 1655 cm^{-1} related to the unsaturated carbonyl stretching band of chalcone group.

Conclusion

Ten new 1,3-diazabicyclo[3.1.0]hex-3-enes bearing a chalcone unit with ether linkage were synthesized for the investigation of their photochromic properties. IR, ^{1}H NMR and ^{13}C NMR characterized the structure of the chalcones and photochromic compounds. All of the bicyclic aziridines reported in this study exhibit good photochromism behavior. Under UV irradiation, these compounds showed both positive and negative photochromism. Also, synthesized ketoaziridines showed photochromic behavior in solution state.

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