Research Article

Journal of Physical Organic Chemistry

Received: 19 September 2008, Revised: 10 February 2009, Accepted: 24 February 2009, Published online in Wiley InterScience: 2009

(www.interscience.wiley.com) DOI 10.1002/poc.1550

Photochromic behavior of several new synthesized bis-1,3-diazabicyclo[3.1.0]hex-3-enes

H. Kiyani[a], N. O. Mahmoodi[a]*, K. Tabatabaeian[a] and M. Zanjanchi[a]

Photochromic compounds (1–6) are synthesized and characterized and the results of their spectra are presented. The structure–photochromic behavior relationship (SPBR) of the synthesized compounds has been analyzed.

Supporting information may be found in the online version of this article.

Keywords: bis1,3-diazabicyclo[3,1,0]hex-3-ene; photochromic; structure–photochromic behavior relationship (SPBR)

INTRODUCTION

Photochromism is defined as light-induced reversible transformation of a chemical species between two isomers having different absorption spectra. The difference in geometry and electronic structure between the two isomers, which is at the origin of the color switch, has also been successfully exploited to reversibly control other properties such as phase behavior of liquid crystals, refractive index, fluorescence, redox potential, electron transfer, and nonlinear optical properties. Although many types of photochromic compounds have been reported so far, crystals that show photochromic reactions in the crystal state are very rare.[1–2] Recently, we became interested in the photochromism and photoproduction of 1,3-diazabicyclo[3.1.0]hex-3-ene derivatives with various substitution.[3–7] Colorless isomers A and B, after remaining for ~5–15 s under ordinary room light, changed color; compound A with NO_2 group in *para* position changed to deep blue (A′ photoisomer) while compound B with NO_2 group in *meta* position changed to pink (B′ photoisomer) (Fig. 1). We herein present 16 new photochromic compounds **A**, **B** (Fig. 1), and **1**–**6** (Scheme 1). These molecules are new derivatives of this well-known photochromic class 1,3-diazabicyclo[3.1.0]hex-3-ene. Applications directly dependent upon the color change caused by the molecular and electronic structures of the two (c = close, o = open) (Fig. 1) or three species (cc, co, oo) (Scheme 4) and their corresponding absorption or emission spectra include the following: variable-transmission optical materials such as photochromic ophthalmic lenses or camera filters; fluid flow visualization; optical information storage; novelty items (toys, T-shirts, etc.); authentication systems (security printing inks); and cosmetics.

Requirements for photonics devices include: (1) thermal stability of both isomers; (2) low fatigue can be cycled many times without loss of performance, repeatable cycle number $> 10^4$; (3) high sensitivity, quantum yield > 0.5; (4) rapid response; (5) non-destructive readout capability; (6) reactivity in the solid state. The more important requirements are thermal stability of both isomers and fatigue resistant character. Recently, we used novel potentiometric as membrane sensors based on 6-(4-nitrophenyl)-2,4-diphenyl-3,5-diazabicyclo[3.1.0] hex-2-ene and 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl-3,5-diazabicyclo[3,1,0] hex-2-ene for detection of Sn (II) [8] and strontium (II) ions[9] at trace levels in real samples, respectively.

Solid-state organic photochromic molecules have attracted much attention due to their potential applications in various optoelectronic devices such as optical memory, optical switches, electronic display, information storage, and so on. Typical examples include *N*-salicylideneanilines, dinitrobenzylpyridines, diphenylmaleonitriles, triarylimidazole dimers, aziridines, diarylethenes, diarylperfluorocyclopentenes, and biindenylidenedione derivatives.[10–13] Among them, 1,3-diazabicyclo[3.1.0]hex-3-ene derivatives synthesized from aziridine moiety are a class of unique photochromic compounds, which generate bistable molecules and undergo photochromism in the crystalline state. This property allows us to consider bicyclic aziridines as possible candidates in the search for radiochromic materials.

RESULTS AND DISCUSSION

Synthesis and photochromic investigations of novel 1,3-diazabicyclo[3.1.0]hex-3-enes

In continuation of prior work in the field of 1,3-diazabicyclo[3.1.0] hex-3-ene systems and their applications in photochromism organic chemistry,[14–16] we now present the synthesis and photochromic investigations of novel bis-1,3-diazabicyclo[3.1.0]hex-3-enes. The structures shown in this contribution possess a variety of functions linked by aryl O-alkyl and O-benzyl spacers (Scheme 2).

Ketoaziridine **7** was prepared starting from chalcone, **8** to facilitate dibrominated **9** at the double bond utilizing bromine in chloroform solution, followed by aziridination with solution of ammonia in absolute ethanol at room temperature (Scheme 3).[3,5,7]

* *Correspondence to: N. O. Mahmoodi, Department of Organic Chemistry, University of Guilan, P.O. Box 1914, Rasht, Iran.*
E-mail: mahmoodi@guilan.ac.ir

a *H. Kiyani, N. O. Mahmoodi, K. Tabatabaeian, M. Zanjanchi*
Department of Organic Chemistry, University of Guilan, Rasht, Iran

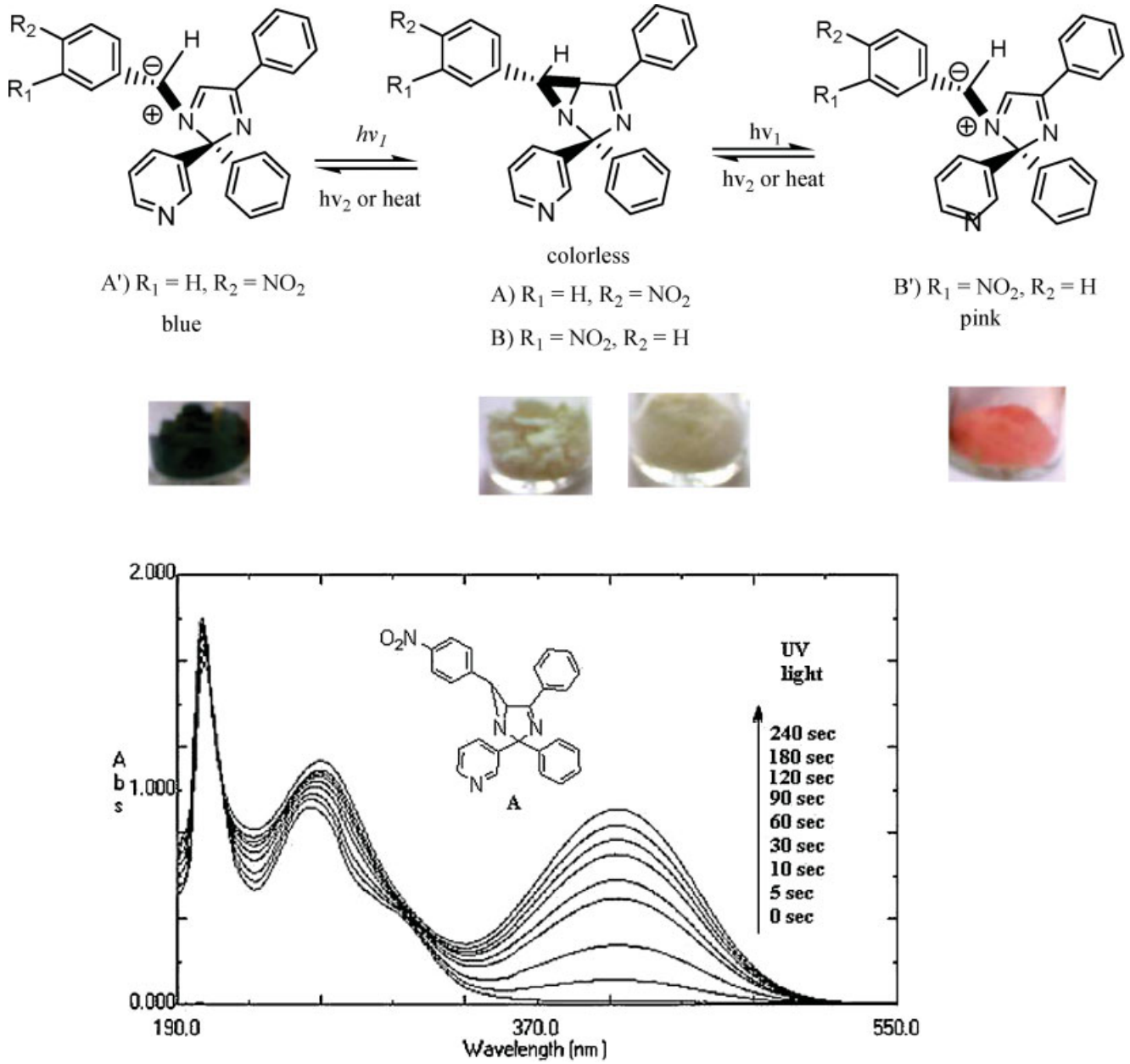


Figure 1. Absorption spectra of 6-(4-nitrophenyl)-2,4-diphenyl-2-(pyridin-2-yl)-1,3-diazabicyclo[3.1.0]hex-3-ene in EtOH ($C = 2.0 \times 10^{-4}$ M) before and after successive UV irradiation (λ_{ex} 315 nm) A closed form (white) upon irradiation with 254 nm light to A′ open form (blue)

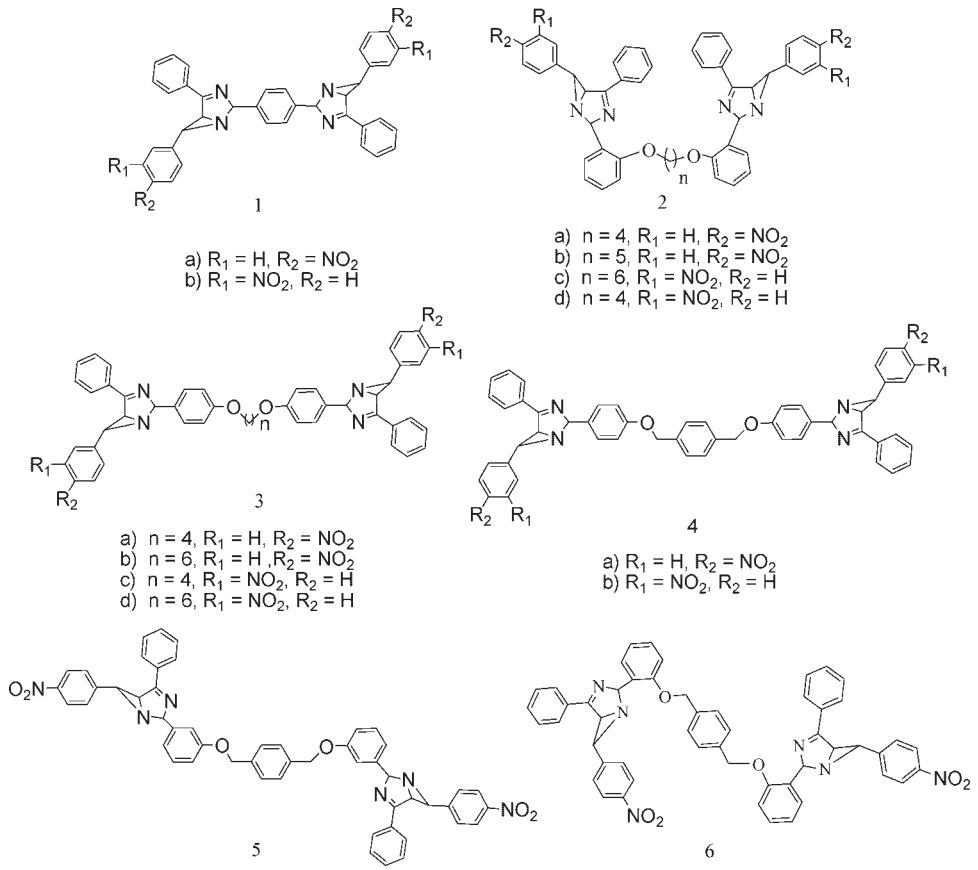
The merits of this system are based on (1) the synthesis of new class of photochromic bicyclic aziridines; (2) the accessible starting materials with prospective of industrial scale; (3) a facile preparation with high percentage yield of products; and (4) preparation of variety of symmetric photochromic bis-1,3-diazabicyclo [3,1,0]hex-3-ene compounds.

These compounds can undergo reversible photocyclization between their close–close ring isomer (cc), close–open ring isomer (co), and open–open ring isomer (oo) under irradiation using a light source of appropriate wavelength. Photoisomerization of these photochromic compounds with a phenyl or arylen bridging unit is illustrated in Scheme 4.

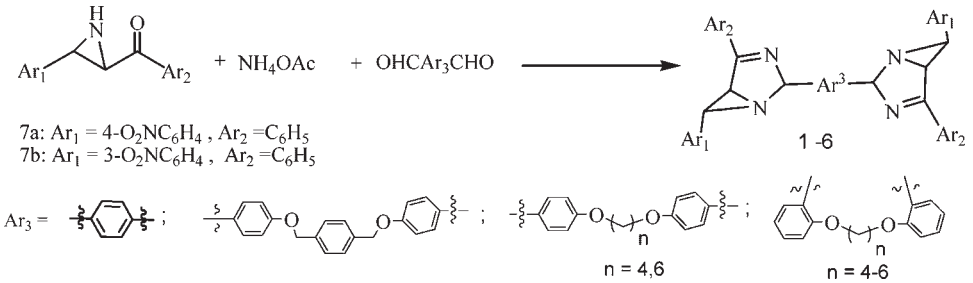
All synthesized **A**, **B**, and **1**–**6** undergo reversible photochromic reactions in a crystalline state during which a ring opening takes place. We have also found that 1,3-diazabicyclo [3,1,0]hex-3-ene systems undergo reversible photochromic reaction with a shorter half-life reaction in cyclohexane, ethanol, acetone, and ethyl acetate by irradiation with 254 nm UV light and visible light. Both the cc-isomer (colorless) and the photogenerated isomer co- or oo-form (colored) is stable at the ambient condition and the coloration/decoloration cycles could be repeated without destruction of the crystals. By increasing the duration of irradiation, the population of the *o*-form in the colored crystals increases, resulting in deepening of their color in the photochromic crystals. The absorption spectra in the range of 200–800 nm (EtOH, $C = 2.0 \times 10^{-4}$ M), as well as position of absorption band maxima for the initial (λ^{A} nm), and photo-induced (λ^{B} nm), were formed upon UV irradiation. The changes in absorption of a bis1,3-diazabicyclo [3,1,0]hex-3-ene **1**–**6** in ethanol at 254 nm are shown in Table 1.

The open form of **1a** after irradiation with UV-light absorbs at longer wavelengths – λ^{B}_{max} is red-shifted down to 261, 405 nm

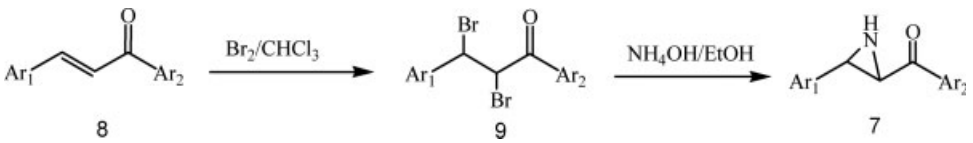
Journal of Physical Organic Chemistry



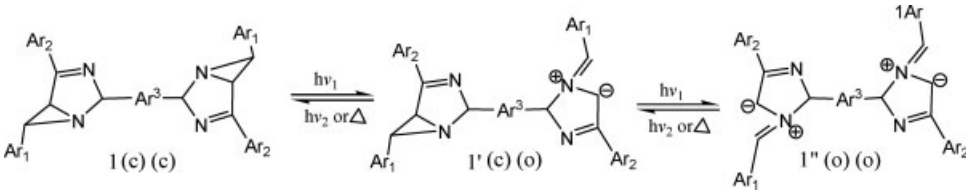
Scheme 1.



Scheme 2. Synthetic route for the preparation of bis compounds 1–6



Scheme 3. Synthetic route for the preparation of aziridines



Scheme 4. Photochromic reactions of 1,3-diazabicyclo [3,1,0]hex-3-ene with phenylene or arylen linkage

Table 1. Spectra and λ^{A}_{max}, λ^{B}_{max}, λ_{ex}, and percent yield of **1–6**

Entry	λ_{ex}, (nm)	λ^{A}_{max}, (nm)	λ^{B}_{max}, (nm)	Yield (%)
1a	238	207, 251	207, 261, 405	82
1b	270	207, 244	207, 262, 360	76
2a	237	298, 230, 248, 275	258, 360, 406	80
2b	246	209, 251	212, 260, 412	85
2c	252	205, 228	205, 283, 376	65
2d	250	220, 246	220, 256, 320, 378	85
3a	257	203, 227, 259	203, 280, 412	74
3b	248	207, 257	207, 269, 415	75
3c	250	215, 228	215, 280, 372	74
3d	260	206, 221	204, 283, 376	71
4a	298	250, 280	206, 406	77
4b	205, 227	205, 283, 374	406	69
5	—	208, 256	208, 224, 264, 408	74
6	284	208, 245	208, 264, 412	55

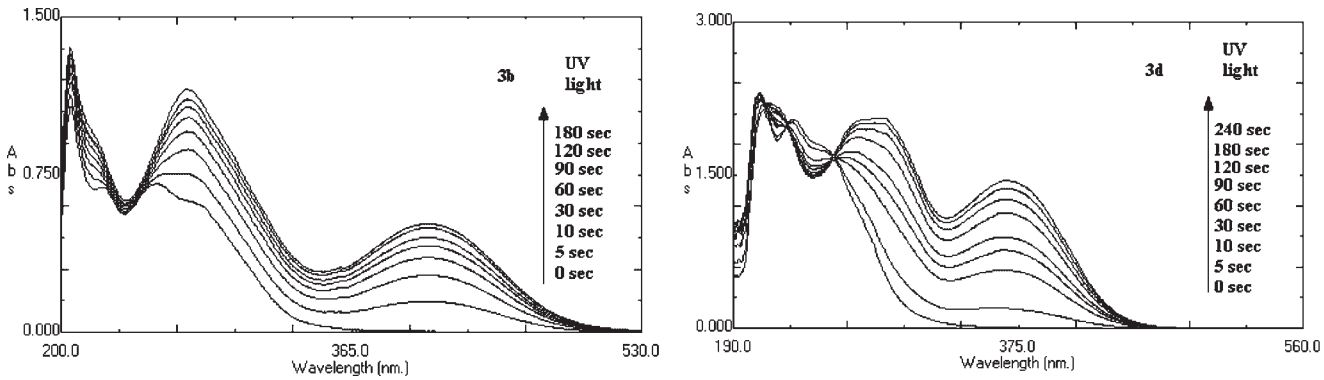


Figure 2. UV–Vis Absorption spectral changes of **3b** and **3d** (cc) upon irradiation under 254 nm light **3b′** and **3d′** (oo) in EtOH ($C = 2.0 \times 10^{-4}$) before and after successive UV irradiation (λ_{ex} 248 and 260 nm), respectively

compared to the λ^{A}_{max} originating at 207, 251 nm (Table 1). Both compounds **1a** and **1b** exhibit acceptable light sensitivity. However, **1a** shows a better photocoloration/photobleaching ratio.

The yield of preparation for compound **3b** is more than **3d;** the open form of **3d** absorbs at slightly shorter wavelengths – λ^{B}_{max} is blue-shifted down to 376 nm compared to **3b** λ^{B}_{max} 415 nm. Both compound **3b** and **3d** exhibit acceptable light-sensitivity and satisfactory photocoloration/photobleaching ratio. Compound **3b** exhibits a higher light sensitivity than **3d** (Fig. 2). The pronounced photochromic behavior of **3b** is attributed to the presence of *para*-NO_2 substitution effect. The ^{13}C NMR of compound **2c** consists of a virtually pure mixture of (cc) and (oo) in a ratio of ~66:34. This is best ascertained by monitoring the total integral for five characteristic signals for (oo) and (cc) isomer.

The ^{1}HNMR of **2c** in the presence of even ordinary room light indicates an interesting photoisomerization reaction and two sets of signals for **2c** (cc): **2c′** (oo) photoisomers with ratio of 66:34 could exist (Figs. 3 and 4).

EXPERIMENTAL

The UV/Vis absorption spectra in the range 200–800 nm (EtOH, $C = 2.10^{-4}$) as well as position of absorption band maxima for the initial **A** (λ^{A}_{max} nm) and photoinduced **A′** ($\lambda^{A'}_{max}$ nm) photoisomers were measured with a Shimadzu UV-2100 spectrophotometer. Chemicals were purchased from Fluka, Merck, and Aldrich. Melting points were uncorrected and determined by Mettler Fp5 melting point apparatus. Products were characterized by ^{1}H, ^{13}C NMR, TLC, and mp). All NMR data were recorded in $CDCl_3$ using a Bruker Avance 500-MHz spectrometer. Chemical shifts are reported in ppm (δ) using deuterated solvents as internal references.

Elemental analyses were made by a Carlo-Erba EA1110 CNNO-S analyzer and agreed with the calculated values. Synthesis of dialdehyde,[17–19] 4-nitrochalcone,[20] 2,3-dibromo-4-nitrochalcone,[5,7] (3-(4-nitrophenyl)aziridin-2-yl)(phenyl) methanone **7a**, and (3-(3-nitrophenyl)aziridin-2-yl)(phenyl)methanone **7b** were prepared according to a standard procedure.[3]

6-(4-nitrophenyl)-2,4-diphenyl-2-(pyridin-3-yl)-1,3-diazabicyclo[3.1.0]hex-3-ene (A): a typical procedure

(3-(4-nitrophenyl)aziridin-2-yl)(phenyl)methanone **7a** (0.268 g, 1 mmol), NH_4Br (0.1 g, 1 mmol), and the appropriate ketone (1 mmol) were dissolved in 6 ml of absolute ethanol and stirred at room temperature. Anhydrous gaseous ammonia was gently blown into the reaction mixture for several hours. Alternatively, instead of gaseous ammonia, 5 mmol NH_4OOCCH_3 was used. In this case, the reaction was completed after 2–4 days instead of 1 week. A color change in the reaction mixture from white to blue

Journal of Physical Organic Chemistry

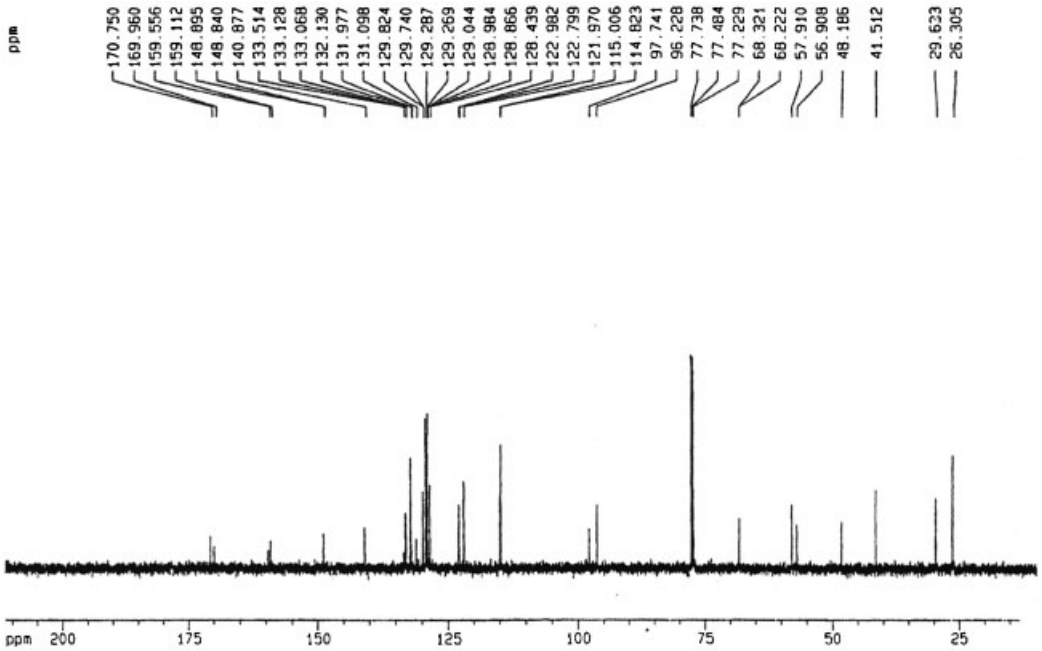


Figure 3. The ^{1}HNMR and ^{13}C NMR of **2c** indicated mixture of two isomers (cc):(oo) in ratio ~ 66:34

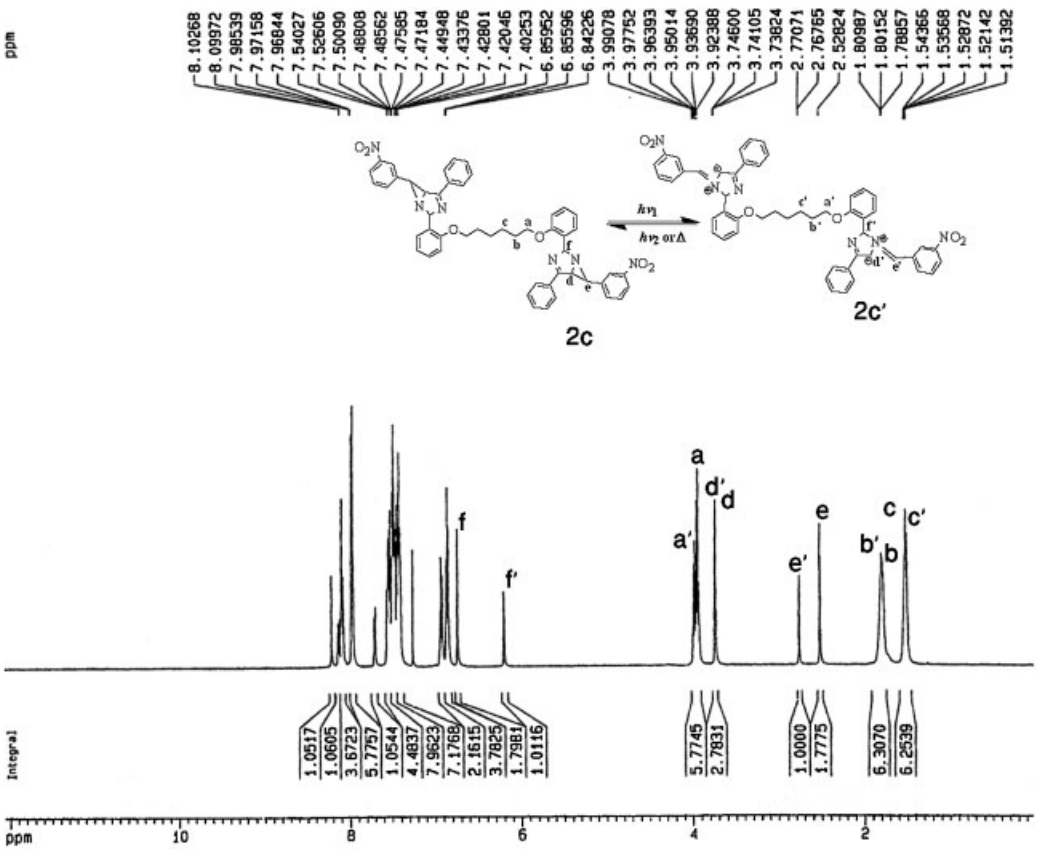


Figure 4. ^{1}HNMR of **2c** indicated mixture of two photoisomers with ratio of 66:34 for **2c** (cc): **2c**′ (oo)

or greenish blue is characteristic for product formation. The reaction mixture was filtered, washed with ethanol, dried in air, and the resulting solid recovered, purified by silica gel column chromatography and recrystallized by ethanol, methanol, or some other suitable solvent. Collected as a white solid. Yield 85%, mp 216–217 °C; closed-form, yield 85%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.6 (s, 1H), 3.77 (s, 1H), 7.06 (m, 1H), 7.21 (t, $J = 8.3$ Hz, 1H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.39–7.68 (m, 7H), 7.90 (d, $J = 7.9$ Hz, 2H), 7.97 (d, $J = 7.90$ Hz, 2H), 8.13 (d, $J = 8.36$ Hz, 2H), 8.50 (d, $J = 4.4$ Hz, 1H). After irradiation with UV light converted to blue (open-form, 15%, A′): ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.54 (s, 1H), 3.92 (s, 1H), 7.06 (m, 1H), 7.25 (t, $J = 7.7$ Hz, 2H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.39–7.68 (m, 5H), 7.90 (d, $J = 7.9$ Hz, 2H), 7.97 (d, $J = 7.90$ Hz, 2H), 8.13 (d, $J = 8.36$ Hz, 2H), 8.61 (d, $J = 4.4$ Hz, 1H).

6-(3-nitrophenyl)-2,4-diphenyl-2-(pyridin-3-yl)-1,3-diazabicyclo[3.1.0]hex-3-ene (B)

A similar procedure as applied for **A** was practical but instead of **7a** same amount of **7b** was utilized. Yield 75%, mp 218–219 °C. Closed-form, 90% ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.63 (d, $J = 1.8$ Hz, 1H), 3.78 (d, $J = 1.8$ Hz, 1H), 7.06 (m, 1H), 7.20 (m, 1H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.40–7.48 (m, 4H), 7.55 (td, $J = 1.5$, 7.9 Hz, 1H), 7.60 (t, $J = 7.7$ Hz, 1H), 7.68 (d, $J = 7.7$ Hz, 1H), 7.91 (d, $J = 7.7$ Hz, 2H), 8.07 (d, $J = 9.2$ Hz, 2H), 8.09 (dd, $J = 1.0$. 7.7 Hz, 1H), 8.17 (s, 1H), 8.52 (t, $J = 4.6$ Hz, 1H). A white solid, after irradiation with UV light converted to pinkish, (open-form, **B**′ 10%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.56 (d, $J = 1.9$ Hz, 1H), 3.92 (d, $J = 1.9$ Hz, 1H), 7.06 (m, 1H), 7.20 (m, 1H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.40–7.48 (m, 4H), 7.55 (td, $J = 1.5$, 7.9 Hz, 1H), 7.60 (t, $J = 7.7$ Hz, 1H), 7.73 (d, $J = 7.7$ Hz, 1H), 7.91 (d, $J = 7.7$ Hz, 2H), 8.07 (d, $J = 9.2$ Hz, 2H), 8.09 (dd, $J = 1.0$. 7.7 Hz, 1H), 8.14 (s, 1H), 8.60 (d, $J = 4.6$ Hz, 1H) ppm.

Preparation of 6-(4-nitrophenyl)-4-(4-(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0] hex-3-en-2-yl)phenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene: a typical procedure (1a; $C_{38}H_{28}N_6O_4$)

(3-(4-nitrophenyl)aziridin-2-yl)(phenyl)methanone **7a** (0.536 g, 2 mmol), NH_4Br (0.2 g, 2 mmol) and the appropriate aldehyde (1 mmol) were dissolved in 10 ml of absolute ethanol and stirred at room temperature. Anhydrous gaseous ammonia is gently blown into reaction mixture for several hours. Alternatively, instead of gaseous ammonia, 10 mmol NH_4OOCCH_3 was used. In this case, the reaction was completed after 3 days instead of 2 weeks. A color was changed from orange into blue or greenish blue for product formation. The reaction mixture was filtered, washed with ethanol, dried in the air, and the resulting solid recovered 0.72 g (yield 82%), mp 211–212 °C, white solid, purified by silica gel column chromatography and recrystallized by ethanol (65.5% yield), methanol, or some other suitable solvent. (**1a**) IR (KBr, ν/cm^{-1}): 3080, 3040, 1600, 1570, 1510, 1340, 1045, 1020, 860, 840, 770, 740, 690. Closed-form, dl, 60%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.54 (s, 2H), 3.84 (s, 2H), 6.84 (s, 2H), 7.52–7.66 (m, 14H), 8.02 (d, $J = 7.4$ Hz, 4H), 8.25 (d, $J = 7.0$ Hz, 4H); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 41.5, 57.7, 96.9, 123.5, 127.6, 127.5, 128.5, 128.6, 128.8, 131.5, 131.7, 140.6, 145.8, 147.2, 170.5. After irradiation with UV light converted to blue, open-form, 40%, dl, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.82 (s, 2H), 3.84 (s, 2H), 6.27 (s, 2H), 7.52–7.66 (m, 14H), 8.02 (d, $J = 7.4$ Hz, 4H), 8.23 (d, $J = 7.5$ Hz, 4H); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 47.5, 56.7, 95.7, 123.5, 127.4, 127.5, 128.5, 128.6, 128.8, 131.5, 131.7, 141.0, 145.9, 147.2, 169.9. Closed-form, meso, 50%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.49 (s, 2H), 3.80 (s, 2H), 6.80 (s, 2H), 7.52–7.66 (m, 14H), 8.02 (d, $J = 7.4$ Hz, 4H), 8.20 (d, $J = 7.5$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 41.4, 57.6, 96.9, 123.5, 127.0, 127.5, 128.5, 128.6, 128.8, 131.4, 131.7, 138.6, 145.7, 147.1, 170.4. Open-form, meso, 50%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.82 (s, 2H), 3.80 (s, 2H), 6.33 (s, 2H), 7.52–7.66 (m, 14H), 8.02 (d, $J = 7.4$ Hz, 4H), 8.23 (d, $J = 7.5$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 47.4, 56.7, 95.7, 123.5, 127.1, 127.5, 128.5, 128.6, 128.8, 131.4, 131.7, 138.2, 145.7, 147.1, 169.5. Anal. Calcd for $C_{38}H_{28}N_6O_4$: C, 72.14; H, 4.46; N, 13.28; found C, 72.17; H, 4.47; N, 13.29.

6-(3-nitrophenyl)-4-(4-(6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)phenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (1b; $C_{38}H_{28}N_6O_4$)

A similar procedure as applied for **1a** was practical but instead of **7a** same amount of **7b** was utilized. Yield 76%, mp 203–204 °C, white solid, IR (KBr, ν/cm^{-1}): 3080, 3050, 1600, 1570, 1515, 1330, 1040, 1020, 835, 770, 740, 690. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.57 (s, 2H), 3.80 (s, 2H), 6.85 (s, 2H), 7.52–7.75 (m, 14H), 7.92–8.00 (m, 4H), 8.12–8.14 (m, 2H), 8.25 (s, 2H); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 41.4, 57.7, 95.9, 121.5, 122.5, 127.1, 128.6, 128.7, 128.9, 129.7, 131.7, 131.9, 140.4, 140.6, 140.7, 148.4, 170.7. After irradiation with UV light converted to pink, open-form, 40%, dl, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.83 (s, 2H), 3.80 (s, 2H), 6.27 (s, 2H), 7.52–7.75 (m, 14H), 7.92–8.00 (m, 4H), 8.12–8.14 (m, 2H), 8.18 (s, 2H); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 47.6, 56.9, 97.3, 121.4, 121.5, 127.2, 128.6, 128.7, 128.9, 129.6, 131.7, 131.9, 140.4, 140.7, 141.2, 148.4, 169.9. Closed-form, meso, 50%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.54 (s, 2H), 3.80 (s, 2H), 6.80 (s, 2H), 7.52–7.75 (m, 14H), 7.92–8.00 (m, 4H), 8.12–8.14 (m, 2H), 8.25 (s, 2H); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 41.3, 57.6, 95.8, 121.5, 122.6, 127.1, 128.6, 128.7, 128.9, 129.6, 131.5, 131.9, 138.8, 140.4, 140.7, 148.4, 170.8; open-form, meso, 50%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.83 (s, 2H), 3.80 (s, 2H), 6.35 (s, 2H), 7.52–7.66 (m, 14H), 7.92–8.00 (m, 4H), 8.12–8.14 (m, 2H), 8.25 (s, 2H); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 47.5, 56.6, 97.2, 121.3, 121.5, 127.2, 127.6, 128.6, 128.7, 128.9, 131.6, 131.9, 138.4, 140.4, 140.7, 148.4, 169.8. Anal. Calcd for $C_{38}H_{28}N_6O_4$: C, 72.14; H, 4.46; N, 13.28; found C, 72.16; H, 4.48; N, 13.28.

Preparation of 4-(2-(4-(2-(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)-phenoxy)butoxy)phenyl)-6-(4-nitrophenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (2a; $C_{48}H_{40}N_6O_6$)

Synthesis of dialdehyde was completed according to the standard procedure.[18–20] Yield 69%, mp 188–189 °C, beige solid, IR (KBr, ν/cm^{-1}): 3060, 3050, 2950, 2890, 1600, 1520, 1490, 1450, 1340, 1230, 1160, 1040, 1020, 860, 840, 758, 690. Closed-form, 60%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm):δ 2.09–2.12 (m, 4H), 2.53 (s, 2H), 3.54 (s, 2H), 4.03–4.16 (m, 4H), 6.83–6.89 (m, 4H), 6.93 (s, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 7.16–7.21 (m, 4H), 7.25 (d, $J = 8.6$ Hz, 4H), 7.37–7.43 (m, 8H), 7.93 (d, $J = 8.5$ Hz, 4H), 8.03 (d, $J = 8.4$ Hz, 4H); after irradiation with UV light converted to blue (open-form, 40%): ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.96–2.03 (m, 4H), 2.55 (s, 2H), 3.56 (s, 2H), 4.03–4.16 (m, 4H), 6.3 (s, 2H), 6.83–6.89 (m, 4H), 7.00 (d, $J = 7.5$ Hz, 2H), 7.16–7.21 (m, 4H), 7.25 (d, $J = 8.6$ Hz, 4H), 7.37–7.43 (m, 8H), 7.93 (d, $J = 8.5$ Hz, 4H), 7.98 (d, $J = 8.5$ Hz, 4H). Anal. Calcd for $C_{48}H_{40}N_6O_6$: C, 72.35; H, 5.06; N, 10.55; found C, 72.36; H, 5.08; N, 10.55.

Preparation of 4-(2-(5-(2-(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)phenoxy)pentyloxy)phenyl)-6-(4-nitrophenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (2b, $C_{49}H_{42}N_6O_6$)

Yield 85%, mp 172–173 °C, pinkish solid, after irradiation with UV light converted to blue; IR (KBr, ν/cm^{-1}): 3070, 3020, 2950, 2890, 1600, 1570, 1520, 1490, 1450, 1340, 1240, 1040, 1020, 740, 690. Closed-form, ^{1}H NMR (500 MHz, $CDCl_3$, ppm):δ 1.92 (t, J = 5.0, 6.7 Hz, 2H), 1.97 (app d, J = 5.0 Hz, 4H), 2.57 (s, 2H), 3.59 (s, 2H), 4.11 (q, J = 5.6 Hz, 4H), 6.91 (q, J = 7.4, 7.9 Hz, 4H), 6.97 (s, 2H), 7.07 (d, J = 7.3 Hz, 2H), 7.25 (d, J = 8.2 Hz, 4H), 7.29 (t, J = 7.9 Hz, 2H), 7.44 (t, J = 7.5 Hz, 4H), 7.52 (t, J = 7.2 Hz, 2H), 7.85 (d, J = 8.5 Hz, 4H), 7.81(d, J = 7.5 Hz, 4H). ^{13}C NMR (125MHz, $CDCl_3$, ppm):δ 23.9, 29.7, 40.7, 57.5, 68.7, 91.9, 11.8, 127.1, 120.5, 123.7, 123.8, 127.13, 127.7, 127.8, 128.3, 128.8, 129.0, 129.2, 130.1, 132.0, 146.3, 157.0, 170.2. Anal. Calcd for $C_{49}H_{42}N_6O_6$: C, 72.58; H, 5.22; N, 10.55; found C, 72.60; H, 5.11; N, 10.56.

6-(3-nitrophenyl)-4-(2-(6-(2-(6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)phenoxy)hexyloxy)phenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (2c, $C_{50}H_{44}N_6O_6$)

As a white solid, yield 65%, mp 143–144 °C. IR (KBr, ν/cm^{-1}): 3080, 3040, 2920, 2860, 1605, 1575, 1530, 1445, 1345, 1242, 1175, 1042, 1022, 830, 770, 735, 690. Closed-form, 66%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.51–1.54 (qui, J = 3.7, 7.4 Hz, 4H), 1.80 (t, J = 6.5 Hz, 4H) 2.53 (s, 2H), 3.74 (s, 2H), 3.94 (t, J = 6.5 Hz, 4H), 6.74 (s, 2H), 6.85 (d, J = 8.6 Hz, 2H), 7.40–7.56 (m, 14H), 7.97 (dt, J = 1.6, 8.4 Hz, 4H), 8.10 (d, J = 1.5 Hz, 2H), 8.21 (d, J = 1.6 Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 26.3, 29.6, 41.5, 57.9, 68.2, 96.2, 114.8, 121.9, 122.8, 128.4, 128.9, 129.0, 129.2, 129.3, 129.7, 131.1, 132.1, 133.1, 140.8, 148.8, 159.1, 107.7. After irradiation with UV light converted to yellow color (open-form, 34%); ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.51–1.54 (qui, J = 3.7, 7.4 Hz, 4H), 1.80 (t, J = 6.5 Hz, 4H), 2.77 (d, J = 1.5 Hz, 2H), 3.75 (d, J = 2.0 Hz, 2H), 3.99 (t, J = 6.6 Hz, 4H), 6.20 (d, J = 2.0 Hz, 2H), 6.92 (d, J = 6.9 Hz, 2H), 6.93 (t, J = 6.7 Hz, 2H), 7.40–7.56 (m, 12H), 7.70 (d, J = 7.7 Hz, 2H), 7.97 (dt, J = 1.6, 7.0 Hz, 4H), 8.08 (s, 2H) 8.14 (dt, J = 1.0, 2.0, 8.2 Hz, 2H). ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 26.3, 29.6, 48.2, 56.9, 68.3, 97.7, 115.0, 122.9, 128.9, 129.8, 129.0, 129.2, 129.3, 131.9, 132.1, 133.0, 133.5, 148.9, 159.5, 169.9. Anal. Calcd for $C_{50}H_{44}N_6O_6$: C, 72.80; H, 5.38; N, 10.19; found C, 72.81; H, 5.40; N, 10.20.

Preparation of 4-(2-(4-(2-(6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)phenoxy)-butoxy)phenyl)-6-(3-nitrophenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (2d, $C_{48}H_{40}N_6O_6$)

Yield 85%, mp 172–173 °C, white solid. IR (KBr, ν/cm^{-1}): 3080, 3020, 2950, 2890, 1600, 1570, 1510, 1450, 1340, 1240, 1045, 1022, 765, 740, 695. Closed-form, 34%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.22 (app t, J = 6.6, 7.3 Hz, 4H), 2.60 (s, 2H), 3.59 (s, 2H), 4.18 (d, J = 3.1 Hz, 4H), 6.83 (s, 2H), 6.86 (d, J = 6.6 Hz, 2H), 6.89 (t, J = 5.6, 8.0 Hz, 2H), 7.05 (dd, J = 1.3, 6.3 Hz, 2H), 7.24 (t, J = 7.1 Hz, 2H), 7.33–7.37 (m, 2H), 7.43–7.52 (m, 8H), 7.96 (dd, J = 1.2, 8.4 Hz, 4H), 8.01 (d, J = 1.4 Hz, 2H), 8.08 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 26.6, 40.5, 47.2, 68.4, 91.8, 112.1, 120.3, 122.2, 122.6, 127.1, 128.8, 128.9, 129.3, 129.7, 130.0, 132.0, 132.3, 133.3, 141.1, 148.6, 156.9, 170.2. After irradiation with UV light converted to pink (open-form, 66%) ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.12 (app t, J = 4.9, 6.8 Hz, 4H), 2.63 (s, 2H), 3.61 (s, 2H), 4.14 (d, J = 5.7 Hz, 4H), 6.83 (s, 2H), 6.86 (d, J = 6.6 Hz, 2H), 6.89 (t, J = 5.6, 8.0 Hz, 2H), 7.08 (dd, J = 1.4, 7.5 Hz, 2H), 7.24 (t, J = 7.0 Hz, 2H), 7.33–7.37 (m, 2H), 7.43–7.52 (m, 8H), 7.96 (dd, J = 1.2, 8.4 Hz, 4H), 8.00 (d, J = 1.2 Hz, 2H), 8.09 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 26.6, 46.7, 57.1, 68.3, 91.9, 112.2, 120.4, 122.3, 122.5, 127.2, 128.8, 129.1, 129.2, 129.7, 129.9, 132.0, 132.2, 133.2, 141.2, 148.8, 157.0, 169.9. Anal. Calcd for $C_{48}H_{40}N_6O_6$: C, 72.35; H, 5.06; N, 10.55; found C, 72.37; H, 5.07; N, 10.56.

6-(4-nitrophenyl)-4-(4-(4-(4-(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)phenoxy)butoxy)-phenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (3a, $C_{48}H_{40}N_6O_6$)

Yield 74%, mp 192–193 °C, beige solid. IR (KBr, ν/cm^{-1}): 3080, 3030, 2950, 2890, 1600, 1510, 1450, 1340, 1242, 1105, 1045, 1020, 830, 770, 740, 695. Closed-form, 60%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.96 (m, 4H), 2.49 (s, 2H), 3.73 (s, 2H), 3.99 (m, 4H), 6.73 (s, 2H), 6.85 (t, J = 7.7 Hz, 4H), 7.38–7.40 (m, 6H), 7.48–7.53 (m, 8H), 7.96 (d, J = 6.8 Hz, 4H), 8.14 (d, J = 8.1 Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 26.4, 41.8, 58.2, 67.8, 96.2, 114.8, 124.0, 127.8, 128.4, 128.8, 128.9, 1293, 131.2, 132.1, 132.2, 147.7, 159.3, 170.7. After irradiation with UV light converted to green (open-form, 40%) ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.96 (m, 4H), 2.75 (s, 2H), 3.73 (s, 2H), 3.99 (m, 4H), 6.20 (s, 2H), 6.92 (t, J = 8.3 Hz, 4H), 7.38–7.40 (m, 6H), 7.48–7.53 (m, 8H), 7.96 (d, J = 6.8 Hz, 4H), 8.20 (d, J = 8.3 Hz, 2H). ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 26.4, 48.4, 57.3, 67.9, 97.7, 115.0, 124.1, 127.7, 128.8, 128.9, 129.0, 129.3, 131.2, 131.9, 132.2, 145.9, 159.1, 169.9. Anal. Calcd for $C_{48}H_{40}N_6O_6$: C, 72.35; H, 5.06; N, 10.55; found: C, 72.38; H, 5.07; N, 10.56.

6-(4-nitrophenyl)-4-(4-(6-(4-(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)phenoxy)-hexyloxy)phenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (3b, $C_{50}H_{44}N_6O_6$)

Yield 75%, mp 167–169 °C, beige solid, IR (KBr, ν/cm^{-1}): 3060, 3040, 2945, 2890, 1600, 1520, 1480, 1450, 1335, 1220, 1108, 1050, 865, 750, 745, 690. Closed-form, 73%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.52 (app t, J = 3.3, 7.0 Hz, 4H), 1.79 (d br, J = 5.9 Hz, 4H) 2.50 (s, 2H), 3.74 (s, 2H), 3.93 (t, J = 6.4 Hz, 4H), 6.74 (s, 2H), 6.84 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 8.2 Hz, 2H), 7.38–7.55 (m, 14H), 7.97 (d, J = 7.2 Hz, 4H), 8.14 (d, J = 8.53 Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 26.3, 29.6, 41.8, 58.2, 68.2, 96.3, 114.8, 124.0, 127.8, 128.4, 128.8, 128.9, 129.3, 131.0, 132.0, 132.2, 146.0, 159.1, 170.0. After irradiation with UV light converted to greenish blue (open-form, 27%): ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.52 (app t, J = 3.3, 7.0 Hz, 4H), 1.79 (d br, J = 5.9 Hz, 4H), 2.76 (s, 2H), 3.73 (s, 2H), 3.97 (t, J = 6.4 Hz, 4H), 6.20 (s, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.93 (t, J = 8.4 Hz, 4H), 7.38–7.55 (m, 14H), 7.97 (d, J = 7.15 Hz, 4H), 8.19 (d, J = 8.6 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 26.3, 29.6, 48.4, 57.3, 68.3, 97.7, 115.0, 124.1, 127.7, 128.8, 129.0, 129.3, 129.3, 131.0, 131.9, 132.2, 147.7, 159.2, 169.9. Anal. Calcd for $C_{50}H_{44}N_6O_6$: C, 72.80; H, 5.38; N, 10.19; found C, 72.82; H, 5.39; N, 10.21.

6-(3-nitrophenyl)-4-(4-(4-(4-(6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)phenoxy)butoxy)phenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (3c, $C_{48}H_{40}N_6O_6$)

Yield 74%, mp 139–140 °C, white solid. IR (KBr, ν/cm^{-1}): 3080, 3020, 2940, 2880, 1605, 1520, 1510, 1345, 1245, 1170, 1045, 1020, 830, 770, 735, 690. Closed-form, 58%, ^{1}H NMR (500 MHz, $CDCl_3$,

ppm): δ 1.95 (qui, $J = 3.3, 6.4$ Hz, 4H), 2.52 (d, $J = 3.0$ Hz, 2H), 3.74 (s, 2H), 4.02 (t, $J = 7.0$ Hz, 4H), 6.73 (d, $J = 3.0$ Hz, 2H), 6.86 (t, $J = 8.7$ Hz, 4H), 7.40–7.56 (m, 14H), 7.98 (d, $J = 7.5$ Hz, 4H), 8.10 (d, $J = 2.0$ Hz, 4H), 8.21 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 26.4, 41.5, 57.9, 67.9, 96.2, 114.8, 115.0, 122.0, 122.8, 128.9, 129.0, 129.3, 129.7, 131.2, 132.1, 133.0, 133.7, 140.8, 148.8, 159.0, 170.8. After irradiation with UV light converted to yellow (open-form, 42%): ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.95 (qui, $J = 3.3, 6.4$Hz, 4H), 2.77 (s, 2H), 3.74 (s, 2H), 4.05 (t, $J = 7.2$ Hz, 4H), 6.20 (d, $J = 3.0$ Hz, 2H), 6.93 (t, $J = 8.7$ Hz, 4H), 7.40–7.56 (m, 12H), 7.70 (d, $J = 7.6$ Hz, 4H), 7.98 (d, $J = 7.5$ Hz, 4H), 8.08 (s, 2H), 8.13 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 26.4, 48.2, 56.9, 68.0, 97.7, 114.9, 115.1, 122.0, 123.0, 128.5, 129.0, 129.1, 129.3, 129.8, 131.2, 132.1, 133.1, 133.7, 140.0, 148.9, 159.4, 169.9. Anal. Calcd for $C_{48}H_{40}N_6O_6$: C, 72.35; H, 5.06; N, 10.55, found C, 72.36; H, 5.08; N, 10.06.

6-(3-nitrophenyl)-4-(4-(6-(4-(6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)phenoxy)-hexyloxy)phenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (3d, $C_{50}H_{44}N_6O_6$)

Yield 71%, mp 170–171 °C, white solid; IR (KBr, ν/cm^{-1}): 3060, 3030, 2950, 2900, 1600, 1518, 1482, 1450, 1340, 1220, 1105, 1040, 860, 750, 740, 690. Closed-form, 70%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.52 (m, 4H), 1.78 (m, 4H) 2.52 (s, 2H), 3.73 (s, 2H), 3.93 (t, $J = 6.4$ Hz, 4H), 6.74 (s, 2H), 6.85 (t, $J = 6.6, 8.2$ Hz, 2H), 7.39–7.45 (m, H), 7.45–7.55 (m, H), 7.97 (d, $J = 7.2$ Hz, 4H), 8.10 (s, 4H), 8.22 (s, 2H); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 26.3, 29.6, 41.5, 57.9, 68.2, 96.3, 114.8, 121.9, 128.4, 128.5, 128.9, 129.0, 129.3, 129.7, 131.1, 132.1, 133.1, 140.8, 148.8, 159.1, 170.7. After irradiation with UV light converted to yellow (open-form, 30%) ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.52 (m, 4H), 1.79 (m, 4H), 2.77 (s, 2H), 3.73 (s, 2H), 3.98 (t, $J = 6.5, 7.0$ Hz, 4H), 6.20 (s, 2H), 6.92 (t, $J = 6.6, 8.2$ Hz, 2H), 6.93 (t, $J = 8.4$ Hz, 4H), 7.39–7.45 (m, H), 7.45–7.55 (m, H), 7.70 (d, $J = 7.4$ Hz, 2H), 7.97 (d, $J = 7.2$ Hz, 4H), 8.08(s, 2H), 8.14 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 26.3, 29.6, 48.2, 56.9, 68.3, 115.0, 121.9, 122.8, 128.4, 128.5, 128.9, 129.0, 129.3, 129.8, 131.0, 132.1, 133.0, 140.9, 148.9, 159.1, 169.9. Anal. Calcd for $C_{50}H_{44}N_6O_6$: C, 72.80; H, 5.38; N, 10.19, found C, 72.82; H, 5.39; N, 10.21.

4-(4-(4-((4-(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo-[3.1.0]hex-3-en-2-yl)phenoxy) methyl)benzyloxy)phenyl)-6-(4-nitrophenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (4a,$C_{52}H_{40}N_6O_6$)

Yield 77%, white solid, mp 165–166 °C; IR (KBr, ν/cm^{-1}): 3080, 3050, 2980, 1600, 1580, 1510, 1445, 1350, 1240, 1170, 1110, 1040, 1020, 770, 740, 690. Closed-form, 60% ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.50 (s, 2H), 3.75 (s, 2H), 5.05 (d, $J = 4.3$ Hz, 4H), 6.74 (s, 2H), 6.93–6.95 (q, $J = 3.5, 8.6$ Hz, 4H), 7.39–7.46 (m, 10H), 7.50 (t, $J = 7.4$ Hz, 4H), 7.53–7.56 (m, 4H), 7.97 (d, $J = 7.1$ Hz, 4H), 8.14 (d, $J = 8.1$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 41.8, 58.2, 70.1, 96.2, 115.2, 124.0, 127.8, 128.3, 128.8, 129.0, 129.2, 131.6, 132.2, 146.0, 147.7, 158.7, 170.7. After irradiation with UV light converted to blue (open-form, 40%) ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.76 (s, 2H), 3.73 (s = 2H), 5.09 (d, $J = 4.1$ Hz, 4H), 6.20 (s, 2H), 6.99–7.02 (q, $J = 3.5, 8.6$ Hz, 4H), 7.39–7.46 (m, 10H), 7.50 (t, $J = 7.4$ Hz, 4H), 7.53–7.56 (m, 4H), 7.97 (d, $J = 7.1$ Hz, 4H), 8.20 (d, $J = 8.7$ Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 48.4, 57.3, 70.1, 97.7, 115.4, 124.1, 127.8, 128.1, 128.5, 128.8, 129.0, 131.9, 132.1, 146.0, 147.8, 158.7, 170.0. Anal. Calcd for $C_{52}H_{40}N_6O_6$: C, 73.92; H, 4.77; N, 9.95; found C, 73.95; H, 4.78; N, 9.97.

4-(4-(4-((4-(6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo-[3.1.0]hex-3-en-2-yl)phenoxy) methyl)benzyloxy)phenyl)-6-(3-nitrophenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (4b, $C_{52}H_{40}N_6O_6$)

Yield 69%, white solid, mp 169–170 °C; IR (KBr, ν/cm^{-1}): 3070, 3050, 2960, 1605, 1580, 1515, 1440, 1345, 1230, 1170, 1040, 1020, 770, 740, 690. Closed-form, 50%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.53 (s, 2H), 3.75 (s, 2H), 5.05 (d, $J = 5.0$ Hz, 4H), 6.75 (s, 2H), 6.93–6.95 (dq, $J = 3.7, 8.6$ Hz, 4H), 7.42–7.54 (m, 16H), 7.56 (d, $J = 7.6$ Hz, 2H), 7.98 (d, $J = 7.4$ Hz, 4H), 8.10 (dt, $J = 3.9, 8.1$ Hz, 2H), 8.22 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 41.6, 57.9, 70.1, 96.2, 115.2, 121.9, 122.8, 128.1, 128.9, 129.0, 129.2, 129.7, 131.6, 132.2, 133.1, 134.0, 137.1, 140.8, 148.8, 158.7, 170.8. After irradiation with UV light converted to yellow, (open-form, 50%) ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.77 (s, 2H), 3.75 (s, 2H), 5.08 (d, $J = 5.0$ Hz, 4H), 6.21 (s, 2H), 6.99–7.02 (dq, $J = 3.7, 8.6$ Hz, 4H), 7.42–7.54 (m, 16H), 7.71 (d, $J = 7.6$ Hz, 2H), 7.98 (d, $J = 7.4$ Hz, 4H), 8.09 (s, 2H), 8.14 (app dt, $J = 8.2$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 48.2, 56.9, 70.2, 97.7, 115.4, 121.9, 123.0, 128.0, 128.5, 128.9, 129.0, 129.3, 129.7, 131.9, 132.1, 133.0, 134.0, 137.2, 140.8, 148.9, 159.2, 170.0. Anal. Calcd for $C_{52}H_{40}N_6O_6$: C, 73.92; H, 4.77; N, 9.95; found C, 73.93; H, 4.77; N, 9.96.

4-(3-(4-((3-(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo-[3.1.0]hex-3-en-2-yl)phenoxy)-methyl)benzyloxy)phenyl)-6-(4-nitrophenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (5, $C_{52}H_{40}N_6O_6$)

Yield 74%, mp 144–145 °C, pinkish solid; IR (KBr, ν/cm^{-1}): 3060, 3030, 2930, 2890, 1600, 1520, 1495, 1450, 1340, 1220, 1050, 1010, 860, 835, 750, 690. Closed-form, 58%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.47 (s, 2H), 3.73 (s, 2H), 5.01 (d, $J = 5.6$ Hz, 4H), 6.75 (s, 2H), 6.89 (dd, $J = 2.1, 6.1$ Hz, 2H), 7.11–7.18 (m, 4H), 7.24 (t, $J = 3.9$ Hz, 4H), 7.47 (d, $J = 7.2$ Hz, 4H), 7.53 (d, $J = 8.1$ Hz, 4H), 7.96 (t, $J = 7.4$ Hz, 4H), 8.14 (dd, $J = 3.5, 8.5$Hz, 4H); ^{13}C NMR (125MHz, $CDCl_3$, ppm): δ 42.0, 58.1, 70.1, 96.4, 114.1, 114.8, 120.4, 124.1, 127.7, 128.2, 128.9, 129.3, 130.1, 131.9, 132.1, 137.1, 140.6, 147.9,159.2, 170.9. After irradiation with UV light converted to green (open-form, 42%): ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.77 (s, 2H), 3.71 (d, $J = 2.3$ Hz, 2H), 5.08 (d, $J = 5.6$ Hz, 4H), 6.21 (d, $J = 2.3$ Hz, H), 6.94 (dd, $J = 2.1, 6.2$ Hz, 2H), 7.11–7.18 (m, 4H), 7.33 (t, $J = 8.2$ Hz, 4H), 7.48 (d, $J = 7.3$ Hz, 4H), 7.53 (d, $J = 8.1$ Hz, 4H), 7.96 (t, $J = 7.5$ Hz, 4H), 8.20 (d, $J = 8.6$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 48.3, 57.3, 70.2, 97.8, 114.1, 114.8, 119.9, 124.1, 127.7, 128.1, 129.0, 129.3, 130.1, 131.8, 132.3, 137.2, 142.8, 145.9, 159.4, 170.3. Anal. Calcd for $C_{52}H_{40}N_6O_6$: C, 73.92; H, 4.77; N, 9.95; found C, 73.95; H, 4.78; N, 9.97.

6-(4-nitrophenyl)-4-(2-((4-((2-(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)phenoxy)-methyl)phenyl)methoxy)phenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene (6), $C_{52}H_{40}N_6O_6$)

Yield 70%, mp 186–187 °C, beige solid; IR (KBr, ν/cm^{-1}): 3080, 3040, 2940, 2890, 1600, 1518, 1495, 1450, 1340, 1220, 1040, 1020, 860, 840, 750, 690. Closed-form, 55%, ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.63 (s, 2H), 3.69 (s, 2H), 5.20 (s, 4H), 6.88–6.93 (m, 40H), 7.02 (s, 2H), 7.13 (t, $J = 6.3$ Hz, 2H), 7.30–7.33 (m, 4H), 7.39 (d, $J = 6.2$ Hz, 4H), 7.43–7.42 (m, H), 8.01 (d, $J = 6.9$ Hz, 4H), 8.05 (d,

$J = 8.7$ Hz, 4H). After irradiation with UV light converted to blue (open-form, 45%): ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.62 (s, 2H), 3.61 (s, 2H), 5.17 (s, 4H), 6.60 (s, 2H), 6.98–7.00 (m, 4H), 7.13 (t, $J = 6.3$ Hz, 2H), 7.30–7.33 (m, 4H), 7.36 (d, $J = 5.8$ Hz, 4H), 7.43–7.42 (m, H), 7.92 (d, $J = 5.3$ Hz, 4H), 8.01 (d, $J = 6.9$ Hz, 4H), 8.14 (d, $J = 5.4$ Hz, 4H). Anal. Calcd for $C_{52}H_{40}N_6O_6$: C, 73.92; H, 4.77; N, 9.95; found C, 73.94; H, 4.77; N, 9.97.

REFERENCES

[1] Y. Chen, M.-L. Pang, K.-G. Cheng, Y. Wang, J. Han, Z.-J. He, J.-B. Meng, *Tetrahedron* **2007**, *63*, 4319–4327. (And references therein).
[2] Eds: H. Durr, H. Bouas-Laurent, *Photochromism. Molecules and Systems*, Elsevier, Amsterdam, **2003**.
[3] N. O. Mahmoodi, M. A. Zanjanchi, H. Kiyani, *J. Chem. Res.* **2004**, *6*, 438–440.
[4] H. Kiyani, N. O. Mahmoodi, K. Tabatabaeian, M. A. Zanjanchi, M. Arvand, B. Sharifzadeh, *Russ. J. Org. Chem.* in press.
[5] N. O. Mahmoodi, H. Kiyani, *Bull. Korean S Chem. Soc.* **2004**, *25*, 1417–1420.
[6] M. R. Yazdanbakhsh, N. O. Mahmoodi, S. Dabiry, *Mendeleev Commun.* **2006**, *3*, 192–194.
[7] N. O. Mahmoodi, M. R. Yazdanbakhsh, H. Kiyani, B. Sharifzadeh, *J. Chin. Chem. Soc.* **2007**, *54*, 635–641.
[8] M. Arvand, M. Moghimi, A. Afshari, N. Mahmoodi, *Anal. Chim. Acta* **2006**, *579*, 102–108.
[9] M. A. Zanjanchi, M. Arvand, A. Islamnezhad, N. O. Mahmoodi, *Talanta* **2007**, *74*, 125–131.
[10] Ed.: M. Irie, *Photo-reactive Materials for Ultra-high Density Optical Memory*, Amsterdam, Elsevier, **1994**.
[11] Eds: J. C. Crano, R. J. Guglielmetti, *Organic Photochromic and Thermochromic Compounds*, Plenum Press, New York, **1999**.
[12] M. Irie, editor, special issue 'Photochromism-memories and switches'. *Chem. Rev.* **2000**, *100*, 1683.
[13] H. Bouas-Laurent, H. Durr, *Pure Appl. Chem.* **2001**, *73*, 639–6665.
[14] M. Irie, S. Kobatak, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 195–210.
[15] V. Viktoria, A. Dyakonenko, O. Shishkin, A. V. Zbruev, S. M. Desenko, *Acta Crystallogr.* **2005**, *E61*, o667–o668.
[16] J. Padwa, S. Smolanoff, I. W. Jun, *J. Chem. Soc. Chem. Commun.* **1972**, 409–410.
[17] P. K. Panda, C.-H. Lee, *Org. Lett.* **2004**, *6*, 671–L 674.
[18] P. K. Panda, C.-H. Lee, *J. Org. Chem.* **2005**, *70*, 3148–L 3156.
[19] J. Kim, L. E. Lindoy, T.-H. Ahn, G.-S. Choi, *Chem. Commun.* **2004**, *34*, 3653–3659.
[20] X. L. Jin, H. Sugihara, K. I. Daika, H. Tateishi, Y. Z. Jin, H. Furuno, J. Inanaga, *Tetrahedron* **2002**, *58*, 8321–8329.

