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Photochemistry of benzene and quinoxaline fused Δ^2-1,2,3-triazolines and their trapping products

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ABSTRACT

The benzene and quinoxaline fused Δ^2-1,2,3-triazolines **1a** and **1b** were synthesized in good yields using Knoevenagel condensation and intramolecular 1,3-dipolar cycloaddition as two of the key reactions. Photolysis (254 nm) of Δ^2-1,2,3-triazoline **1a** or **1b** in acetonitrile led to the homolytic cleavage of nitrogen that generated diethyl diazomalonate **7**, highly reactive intermediates aziridines **8a**,**b**, and isoindoles **B**. The latter two species subsequently underwent rearrangement to give the nitrogen extrusion products **9a**,**b**, and polymers. Furthermore, the reactive intermediates were trapped by dienophiles to give the corresponding cycloadducts. Subsequent rearrangement of the *N*-bridged cycloadducts gave *N*-substituted pyrrolo[3,4-*b*]quinoxalines **12b** and **15b** in 6% and 9% yields, respectively. Irradiation of **1a** in the presence of fumaronitrile led to the isolation of cycloadduct **16a** with retention of stereochemistry. Thermal reaction of **1b** gave more nitrogen extruded product **9b** (58–63% yield) than that by photolysis (5–23% yield), which implied that zwitterionic intermediate might be involved in the former.

1. Introduction

The annulation of heteroaromatic compounds or benzene to isoindoles[1] makes them reactive dienes that undergo Diels–Alder reaction with dienophiles to form various cycloadducts. Accordingly, *iso*-condensed heteroaromatic pyrrole derivatives have been frequently used in the research fields of conducting polymers,[2a] organic light emitting diodes,[2b] organic field effect transistors,[2c] and metal ion sensors.[2d] The 1,3-dipolar cycloaddition reaction is one of the most useful synthetic methods to construct five membered heterocycles. The intramolecular 1,3-dipolar cycloaddition of an aromatic azide with an alkene forms an aromatic fused triazolines,[3] which can be used in the synthesis of various alkaloids through thermolysis of the triazolines to extrude a nitrogen and formation of the aziridine intermediates.[4]

Although numerous efforts have been devoted to the synthesis and reaction of heteroaromatic fused 1,2,3-triazolines,[5–8] the mechanism in the thermolysis of these triazolines that leads to the loss of nitrogen remains to be established. Based on experimental results and density functional theory calculation, Feldman et al.[5] proposed that azatrimethylenemethane (ATMM) diyls (Scheme 1a), a nitrogen version of the classical trimethylenemethane (TMM) biradicals,[6] were involved in the thermolysis of 2-(allenyl)phenyl azides. On the other hand, Chiba[7a] and one of us[7b] favored the formation of zwitterionic intermediates in the thermolysis of some triazolines that led to isoindoles or 1,2-dihydroisoquinolines (Schemes 1b and 1c). Based on theoretical calculations, Wladkowsk, Michejda,[7c] and Shea[7d] supported a heterolytic cleavage of the N–N bond in the thermolysis of protonated triazolines or torsionally strained triazolines. In the thermolysis of adducts from azide anion to allenyl esters, Huang[8a] proposed both biradical and zwitterionic intermediates to rationalize their experimental results; however, Smith and co-workers favored zwitterionic intermediates (Scheme 1d) based on sensitive product variation to solvent polarity.[8b]

Compared to the popularity in the thermolysis of aromatic fused triazolines, reports on the photochemistry of triazolines are still rare.[9] Based on stereoselective product distributions as well as high quantum yields of the photoreactions of phenyl triazolines, the mechanism of a one-step expulsion of nitrogen to give a singlet 1,3-diradical rather than a path involving a 1,5-diradical was favored.[9a–c,f] Our results, however, showed that 1,5-diradical was initially formed during the photolysis (vide infra), which was then converted to 1,3-diradical or trapped by dienophiles to various products. Results from the thermolysis of the 4,4-dicarbolylate substituted triazolines seem to involve a zwitterionic intermediates. Herein, we report the synthesis of quinoxaline fused triazoline **1b**, the preparation of benzo-fused triazoline **1a**,[10] and their photochemistry and trapping of reactive intermediates.

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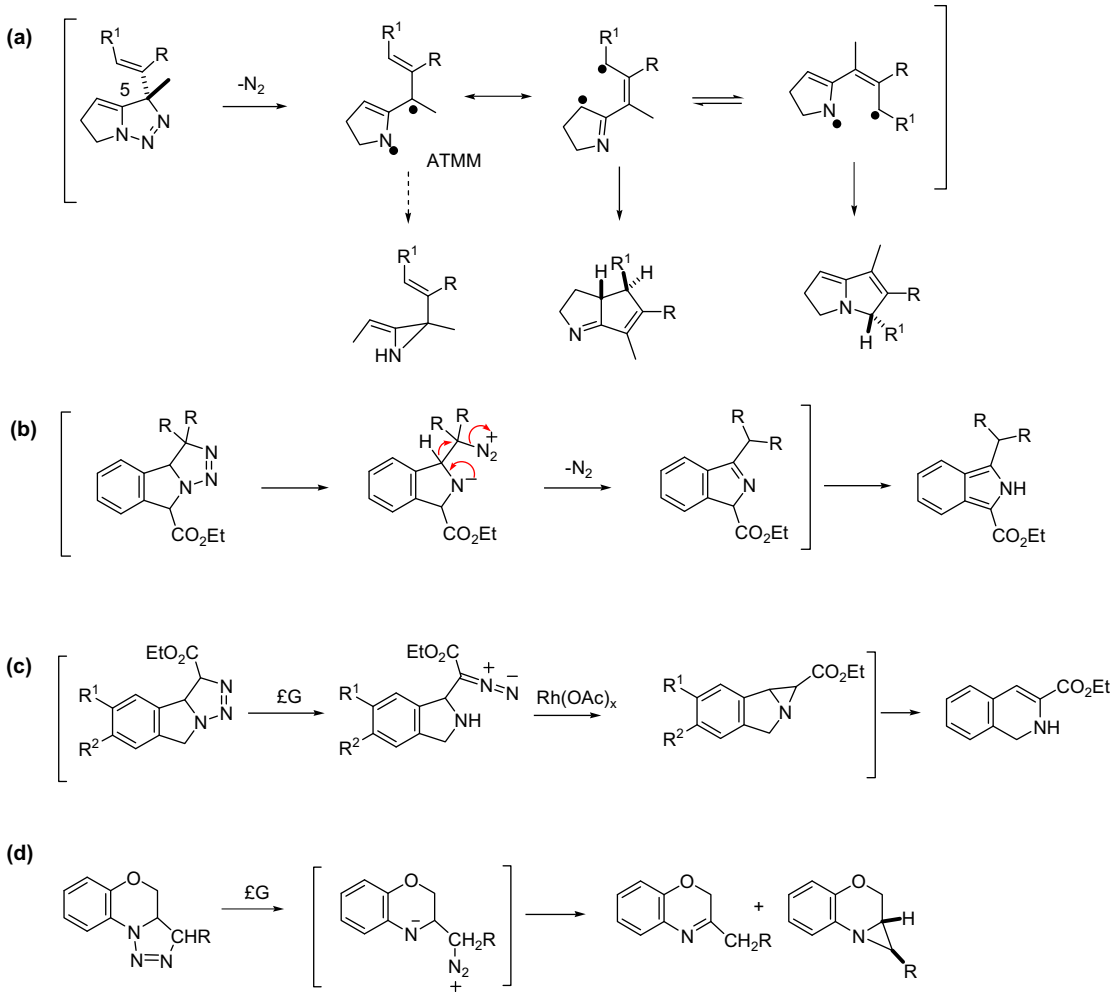
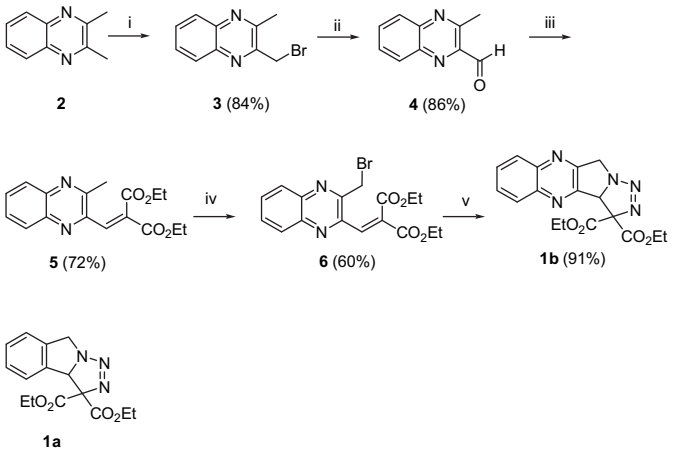


Scheme 1. Literature proposed reaction mechanisms in the thermolysis of Δ^2-1,2,3-triazolines: (a) Ref. 5a, (b) Ref. 7a, (c) Ref. 7b, and (d) Ref. 8b.

2. Results and discussion

Triazolines **1a** was prepared according to literature procedures.[10] The synthetic pathway for triazoline **1b** is depicted in Scheme 2.[11d] Bromination of the readily available 2,3-dimethylquinoxaline with *N*-bromosuccinimide (NBS) in the presence of dibenzoyl peroxide gave **3** in 84% yield.[12] Oxidation of compound **3** by the sodium salt of 2-nitropropane in methanol gave the aldehyde **4** in 86% yield.[13] Knoevenagel condensation of compound **4** with diethyl malonate afforded the alkylidenemalonate **5** in 72% yield.[14] Subsequent bromination of **5** with NBS gave bromoalkylidenemalonate **6** in 60% yield. Treatment of **6** with sodium azide led to the displacement of bromide by azide. Subsequent intramolecular 1,3-dipolar cycloaddition of the azide group to the olefin gave triazoline **1b** in 91% yield.



Scheme 2. Synthesis of quinoxaline fused Δ^2-1,2,3-triazoline **1b**. Reagents and conditions: (i) NBS, dibenzoyl peroxide, *o*-dichlorobenzene, 60 °C, 2.5 h; (ii) $[(CH_3)_2CNO_2]^-Na^+$, MeOH, rt, 6 h; (iii) $CH_2(CO_2Et)_2$, piperidine, AcOH, PhH, reflux, 12 h; (iv) NBS, dibenzoyl peroxide, *o*-dichlorobenzene, 40 °C, 12 h; (v) NaN_3, EtOH, rt, 12 h.

The formation of **1b** from **6** could be monitored by ^{1}H NMR. The disappearance of the methylene protons in **6** at 4.8 ppm and the appearance of two doublets of **1b** at 4.9 and 5.6 ppm (J=17.4 Hz) were observed. The signal of methylene carbon also downfield shifted from 30.3 ppm in bromide **6** to 53.8 ppm in triazoline **1b**. In addition, the signal of alkylidine proton in **6** at 8.1 ppm disappeared and a new signal of a methine proton appeared at 5.9 ppm in **1b**. All spectroscopic data supported that an intramolecular 1,3-dipolar cycloaddition of azide and alkene occurred. However, the newly created chiral center on triazoline **1b** made the ^{1}H NMR spectrum a bit complex. HRMS also supported the formation of triazoline **1b**.

The Uv–vis absorption of triazolines **1a** and **1b** in acetonitrile showed a λ_{max} at 249 nm (ε=6.5×10^3 M^{-1}cm^{-1}) and 239 nm (ε=2.9×10^4 M^{-1}cm^{-1}), respectively. Triazoline **1a** or **1b** (0.025 M in CD_3CN) was photolyzed in Rayonet photoreactor (254 nm) under degassed condition at room temperature. To follow the reaction closely, we took ^{1}H NMR of the samples with different irradiation periods.

After irradiation for ca. 15 min, some changes in the ^{1}H NMR spectra of both **1a** and **1b** were observed. A significant new triplet signal appeared at ca. 0.7 ppm (see Figs. 1 and 2). These triplets were likely due to the aziridine intermediates **8a**,**b**[9] that were formed by the photo-extrusion of nitrogen from the triazolines. Some other changes of signals also appeared, which were consistent with the formation of **7** and **9a** or **9b**; however, parts of the signals were severely overlapped with the starting materials. Similar phenomenon was observed when d_8-THF, $CDCl_3$, and CD_3CN/CD_3OD (v/v=1/4) were used as the solvents in the photolysis (Supplementary data). Even with repeated column chromatography, we failed to isolate the putative aziridine intermediates[9,15] **8a** and **8b**; however, the diethyl diazomalonate **7** and nitrogen extrusion products **9a** and **9b** were isolated (Scheme 3). Compounds **9a** and **9b** were unstable in chloroform; however, they lived long enough for spectral identification.

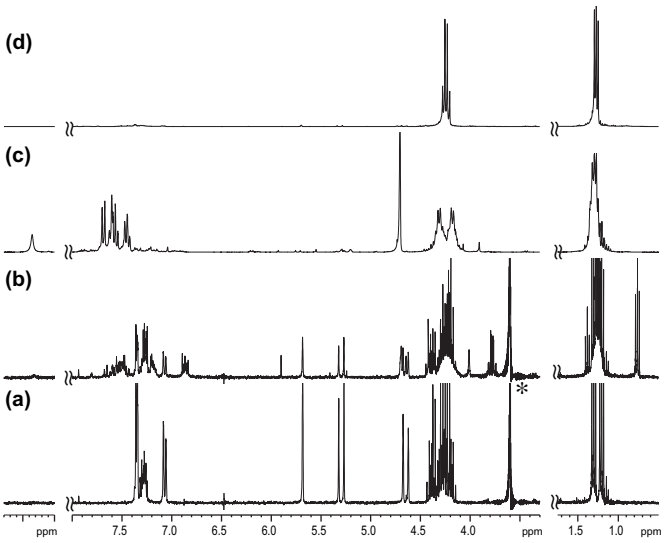


Figure 1. ^{1}H NMR spectra of (a) triazoline **1a** (0.025 M in CD_3CN), and (b) **1a** after irradiated (254 nm) for 15 min, (c) **9a** (in CD_3CN), and (d) **7** (in CD_3CN); where * denotes an internal standard 1,4-dioxane, and the signals around 0.7 ppm were from aziridines **8a**.

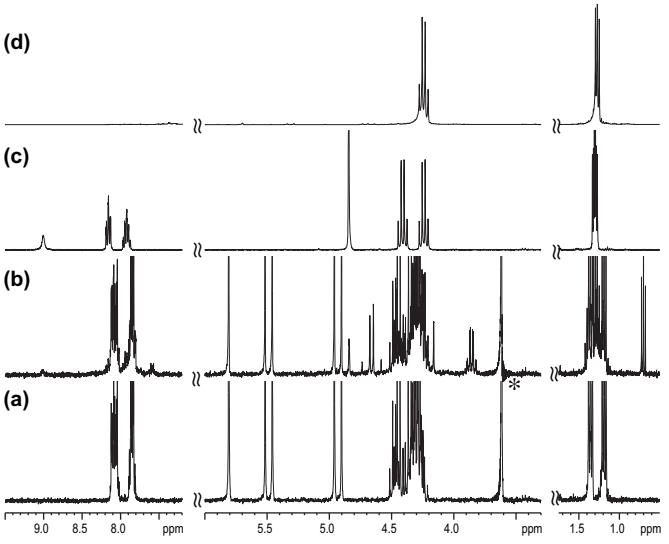
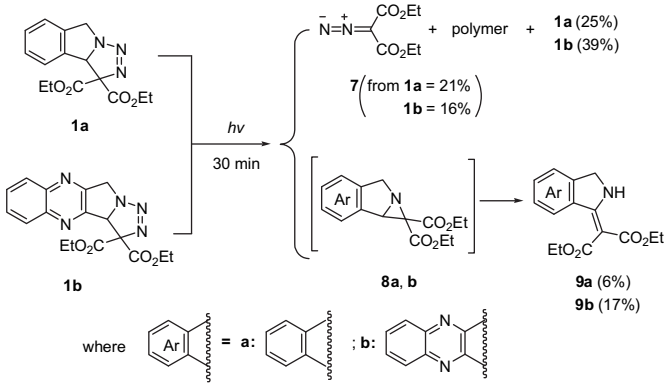


Figure 2. ^{1}H NMR spectra of (a) triazoline **1b** (0.025 M in CD_3CN), and (b) **1b** after irradiated (254 nm) for 15 min, (c) **9b** (in CD_3CN), and (d) **7** (in CD_3CN); where * denotes an internal standard 1,4-dioxane, and the signals around 0.7 ppm were from aziridines **8b**.

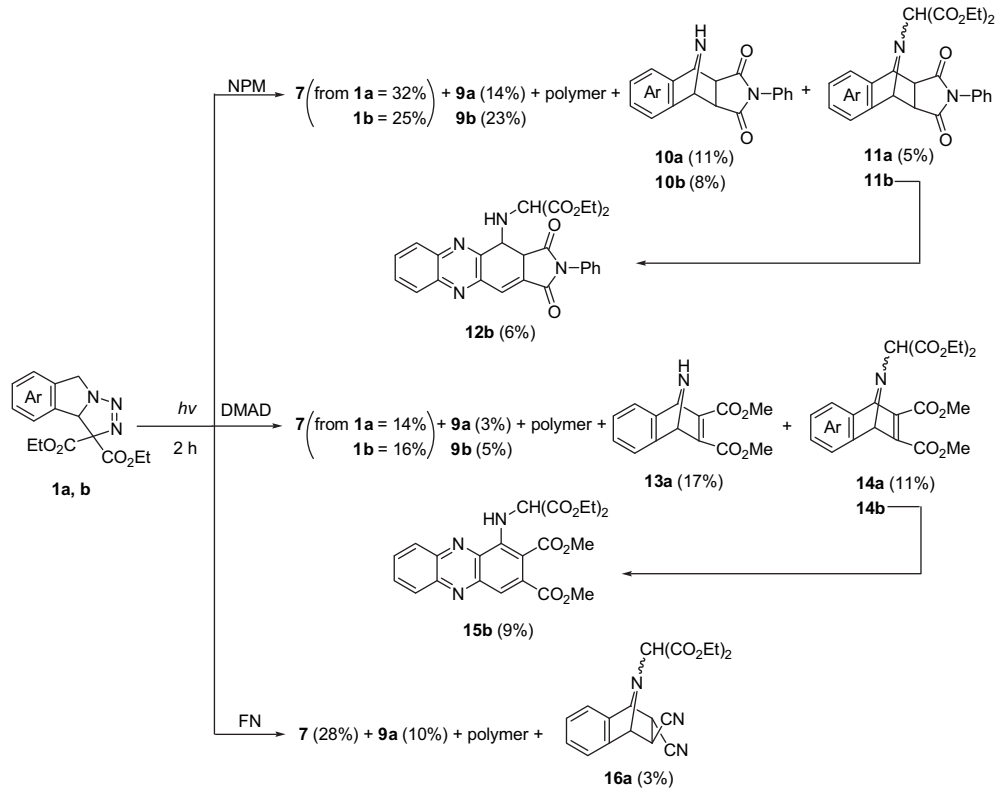


Scheme 3. Photochemical products from the photolysis of triazolines **1a** and **1b**.

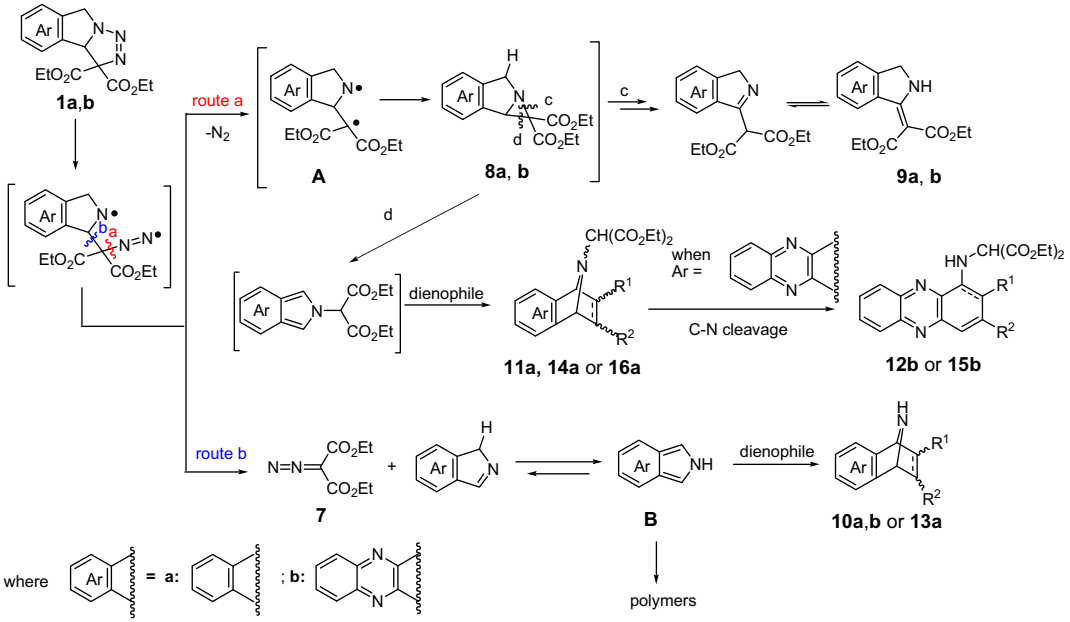
To gain insight into the mechanism of the photo reaction, triazoline **1a** or **1b** was photolyzed in the presence of dienophiles to trap the intermediates involved. Using acetonitrile as the solvent, in the presence of 3 equiv of *N*-phenylmaleimide (NPM) as dienophile, the diethyl diazomalonate **7** and diethyl 2-(2,3-dihydropyrrolo[3,4-*b*]quinoxalin-1-ylidene)malonates **9a**,**b** were formed, along with the Diels–Alder adducts **10a** and **11a** (for **1a**) or **10b** and **12b** (for **1b**) and other unidentified side products. For example, when **1a** was photolyzed in the presence of NPM for 2 h, the reaction products analyzed by HPLC included: diethyl diazomalonate **7** (32%), **9a** (14%), *N*-H-cycloadduct **10a** (11%) and *N*-substituted-cycloadduct **11a** (5%) (Scheme 4). Similar types of reaction products were found when **1a** or **1b** was photolyzed in the presence of excess dimethyl acetylenedicarboxylate (DMAD). Notably, photolysis of **1b** in the presence of dienophiles did not afford the cycloadducts **11b** and **14b**, which were expected from the trapping of *N*-substituted pyrrolo[3,4-*b*]quinoxaline with dienophiles. Instead, compounds **12b** and **15b** were observed, which were associated with the breaking of the *N*-bridge (Scheme 4). Moreover, products from the irradiation of **1a** with fumaronitrile (FN) gave a trapping product **16a** with retention of stereochemistry. The stereochemistry of the *exo*-**10b** and *endo*-**11a** was determined based on those established on a thieno[2,3-*c*]pyrrole system.[11b,c,e]

Photolysis of Δ^2-1,2,3-triazolines in general involves the homolytic extrusion of nitrogen to form 1,3-diradical **A**, which then recombines to form aziridine intermediates **8a**,**b**.[9] The 1,3-diradical **A** was extremely short lived, which has been eluded for EPR detection. Nevertheless, we were able to obtain EPR[16] signals of monoradicals when a glassy matrix of **1a** or **1b** in 2-methyltetrahydrofuran (MTHF) at 77 K was irradiated (230−325 nm), the corresponding signals appeared at 3423 G for **1a** and at 3435 G for **1b**, respectively. Thus, EPR experiments proved the involvement of radical intermediates in the process. Based on the experimental results, we proposed the mechanism as follows. Photolysis of **1a** or **1b** by route a (Scheme 5) led to the formation of aziridine **8a** or **8b**, owing to the high strain energy of **8**, it either underwent ring opening reaction to form compound **9a** or **9b** (through pathway c) or was first converted into the *N*-substituted *iso*-condensed heteroaromatic pyrroles (pathway d) and then trapped by dienophiles to form cycloaddition adducts **11a**, **12b**, **14a**, **15b** and **16a**. Alternatively, photolysis of triazolines **1a** and **1b** may initially underwent an homolysis of the N–N bond followed by nitrogen extrusion to form diethyl diazomalonate **7** and isoindole/pyrrolo[3,4-*b*]-quinoxaline **B**. The reactive isoindoles or pyrrolo[3,4-*b*]-quinoxaline intermediates could further react with dienophiles to give Diels–Alder adducts (Scheme 5, route b) or it may undergo polymerization as well.[17]

We also studied the thermal reaction of triazoline **1b** and the results are shown in Scheme 6. Heating triazoline **1b** alone in benzene at reflux for 24 h gave products **7** (18%) and **9b** (63%).

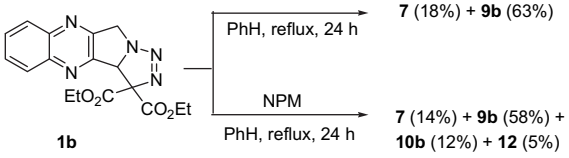


Scheme 4. Photochemical products from the photolysis of triazolines **1a** and **1b** in the presence of various dienophiles.



Scheme 5. Proposed mechanism for photochemistry of heteroaromatic contains triazolines **1a** and **1b**.

Thermolysis of **1b** with NPM in the same conditions also gave the same four products as did the photolysis: diethyl diazomalonate **7** (14%), nitrogen extrusion compound **9b** (58%), *N*-H-cycloadduct **10b** (12%), and the *N*-substituted-cycloadduct **12b** (5%). The results were similar to those reported in literatures,[7c,d,9] indicating the involvement of intermediate **8** and the fragmentation to form diethyl diazomalonate **7**.[7a,8] The thermolysis of triazoline **1b**



Scheme 6. Thermolysis of triazoline **1b** with and without NPM (3 equiv) in benzene.

perhaps went through zwittzerionic intermediate, which led to higher yield of diethyl 2-(2,3-dihydropyrrolo[3,4-*b*]quinoxalin-1-ylidene)-malonates **9b**. Thus, **9b** was obtained in 63% yield by thermolysis but was only 17% by photolysis. Furthermore, thermolysis of triazoline **1b** gave cleaner products with higher yields, whereas, the photolysis which involved 1,3-diradical gave various unidentified polymers as side products.

3. Conclusion

In conclusion, Δ^2-1,2,3-triazoline **1b** can be readily synthesized in five steps. The photochemistry of triazoline derivatives **1a** and **1b** in acetonitrile was studied. Although photolysis of **1a** and **1b** led to complicated reaction products, the Diels–Alder adducts and their rearranged products could be successfully isolated and characterized. Based on these results, we proposed that the photolysis of triazolines **1a** and **1b** underwent homolysis of the N–N bond first to form a 1,5-diradical, which was then converted into the 1,3-diradical **A** by the extrusion of nitrogen. The resultant 1,3-diradical **A** instantly formed the aziridine intermediate **8**, which was then converted into the unstable iso-condensed heteroaromatic pyrrole or immediately gave the rearranged product **9**. Alternatively, the incipient 1,5-diradical gave isoindole derivative **B** along with diethyl diazomalonate **7**. Thermal reaction of **1b** presumably went through zwitterionic intermediates,[11] therefore, it gave cleaner products with higher yields; in contrast, the photolysis which involved 1,3-diradical, gave similar reaction products but with some unidentified polymers as side products.

4. Experimental

4.1. General

Flash column chromatography was performed using silica gel (70–230 mesh). Melting points were determined on a Yanaco MP500D apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75.4 MHz, respectively, with $CDCl_3$ (δ 7.26) or TMS (δ 0.00) as an internal standard. Mass spectra were recorded at electron ionization or FAB mode. Compounds **1a**[10] and **7**[10] were prepared according to literature procedures. Compound **1b** was first reported by Li, however, no spectral data were available.[11d] All reported yields in this work were isolated yields.

*4.1.1. Diethyl 3aH-[1,2,3]triazolo[5,1-a]isoindole-3,3-(8H)-dicarboxylate, **1a**.* A mixture of diethyl 2-(2-(bromomethyl)benzylidene)-malonate[10] (0.45 g, 1.32 mmol) and sodium azide (0.26 g, 3.96 mmol) in 12 mL of methanol/water (v/v=3/1) was stirred at room temperature for 3 h. The reaction mixture was treated with water (20 mL) and dichloromethane (3×10 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was column chromatographed using hexane/ethyl acetate (2:1) as eluent to give 1a (0.37 g, 92%) as a white solid; mp 99–101 °C; R_f=0.58 (hexane/ethyl acetate=2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (t, J=7.3 Hz, 3H), 1.37 (t, J=7.3 Hz, 3H), 4.15–4.48 (m, 4H), 4.68 (d, J=15.5 Hz, 1H), 5.34 (d, J=15.5 Hz, 1H), 5.72 (s, 1H), 7.11 (d, J=7.2 Hz, 1H), 7.20–7.40 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7 (CH_3), 13.9 (CH_3), 55.0 (CH_2), 62.4 (CH_2), 63.3 (CH_2), 68.1 (CH), 95.0 (Cq), 123.0 (CH), 123.3 (CH), 127.7 (CH), 129.1 (CH), 135.9 (Cq), 137.5 (Cq), 164.4 (Cq), 164.9 (Cq); FABMS m/z 304 ($M+H^+$); HR-FABMS ($M+H^+$) m/z calcd for $C_{15}H_{18}N_3O_4$ 304.1292, found 304.1301.

*4.1.2. Preparation of 2-(bromomethyl)-3-methylquinoxaline, **3**.* 2,3-Dimethylquinoxaline 2 (0.40 g, 2.53 mmol), *N*-bromosuccinimide (0.60 g, 3.33 mmol), and dibenzoyl peroxide (0.01 g, 0.04 mmol) was dissolved in 30 mL of 1,2-dichlorobenzene under nitrogen. The reaction mixture was heated to 60 °C and stirred for 2.5 h. After cooling to room temperature, the reaction mixture was passed through a short silica gel column and washed with hexane to remove 1,2-dichlorobenzene. After concentration under reduced pressure, the residue was column chromatographed using hexane/ethyl acetate (7:1) as eluent to give 3 (0.50 g, 84%) as a white solid; mp 120–122 °C; R_f=0.30 (hexane/ethyl acetate=6:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.89 (s, 3H), 4.76 (s, 2H), 7.69–7.78 (m, 2H), 8.01–8.05 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4 (CH_3), 31.8 (CH_2), 128.4 (CH), 129.0 (CH), 129.4 (CH), 130.4 (CH), 140.8 (Cq), 141.9 (Cq), 150.8 (Cq), 153.1 (Cq); EIMS m/z 328/326 (M^+, 24/24), 157 (100); HR-EIMS m/z calcd for $C_{10}H_9^{79}BrN_2$ 235.9949, found 235.9956.

*4.1.3. Preparation of 3-methylquinoxaline-2-carbaldehyde, **4**.* A mixture of 2-nitropropane (0.11 g, 1.24 mmol) and sodium methoxide (0.09 g, 1.67 mmol) in 10 mL of methanol was heated to reflux for 30 min and then cooled to room temperature. Compound **3** (0.21 g, 0.89 mmol) was added and the reaction mixture was stirred at room temperature for 4 h. After removal of the solvent by rotary evaporator, the residue was partitioned between water (45 mL) and dichloromethane (3×15 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was column chromatographed using hexane/ethyl acetate (8:1) as eluent to give **4** (0.13 g, 86%) as a yellow solid; mp 128–130 °C; R_f=0.35 (hexane/ethyl acetate=6:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.05 (s, 3H), 7.79–7.94 (m, 2H), 8.09–8.23 (m, 2H), 10.3 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.2 (CH_3), 128.6 (CH), 130.0 (CH), 130.0 (CH), 133.0 (CH), 140.8 (Cq), 142.7 (Cq), 145.2 (Cq), 153.5 (Cq), 194.0 (Cq); EIMS m/z 172 (M^+, 90), 144 (79), 143 (100), 102 (62); HR-EIMS m/z calcd for $C_{10}H_8N_2O$ 172.0637, found 172.0632.

*4.1.4. Preparation of diethyl 2-((3-methylquinoxalin-2-yl)methylene)-malonate, **5**.* A stirred mixture of aldehyde 4 (1.51 g, 8.78 mmol), diethyl malonate (1.90 g, 11.9 mmol), piperidine (172 mg, 2.02 mmol), and glacial acetic acid (89.0 mg, 1.48 mmol) in 40 mL of dry benzene was heated to reflux for 12 h using a Dean–Stark trap. The solvent was removed by rotary evaporator and the crude products were column chromatographed using hexane/ethyl acetate (3:1) as eluent to give 5 (1.98 g, 72%) as a yellow solid; mp 105–107 °C; R_f=0.28 (hexane/ethyl acetate=3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, J=7.2 Hz, 3H), 1.38 (t, J=7.2 Hz, 3H), 2.89 (s, 3H), 4.38 (q, J=7.2 Hz, 2H), 4.45 (q, J=7.2 Hz, 2H), 7.68–7.80 (m, 2H), 7.92–8.00 (m, 2H), 8.03 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.6 (CH_3), 61.4 (CH_2), 62.1 (CH_2), 128.4 (CH), 129.3 (CH), 129.6 (CH), 131.1 (CH), 132.4 (Cq), 134.8 (CH), 140.7 (Cq), 141.9 (Cq), 145.8 (Cq), 153.1 (Cq), 163.5 (Cq), 166.0 (Cq); EIMS m/z 314 (M^+, 53), 285 (33), 269 (38), 241 (100); HR-EIMS m/z calcd for $C_{17}H_{87}N_2O_4$ 314.1267, found 314.1265.

*4.1.5. Preparation of diethyl 2-((3-(bromomethyl)-quinoxalin-2-yl)-methylene)malonate, **6**.* A mixture of 5 (0.63 g, 2.01 mmol), *N*-bromosuccinimide (0.47 g, 2.49 mmol) and dibenzoyl peroxide (78.0 mg, 0.03 mmol) was dissolved in 35 mL of 1,2-dichlorobenzene under nitrogen. The reaction mixture was stirred at 40 °C for 12 h and then cooled to room temperature. The reaction mixture was passed through a short silica gel column and washed with hexane to remove 1,2-dichlorobenzene, then eluted with dichloromethane. After removal of the solvent under reduced pressure, the residue was column chromatographed using hexane/ethyl acetate (8:1) as eluent to give 6 (0.47 g, 60%) as a black solid; mp 101–103 °C; R_f=0.23 (hexane/ethyl acetate=6:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, J=6.9 Hz, 3H), 1.39 (t, J=7.2 Hz, 3H), 4.39 (q, J=7.2 Hz, 2H), 4.46 (q, J=7.2 Hz, 2H), 4.85 (s, 2H), 7.76–7.81 (m, 2H), 7.95–8.05 (m, 2H), 8.12 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0 (CH_3), 14.0 (CH_3), 30.3 (CH_2), 61.4 (CH_2), 62.1 (CH_2), 129.0 (CH), 129.2 (CH), 131.0 (CH), 131.5 (CH), 132.6 (Cq), 133.7 (CH), 141.3 (Cq), 141.4 (Cq), 145.4 (Cq), 150.7 (Cq), 163.3 (Cq), 165.8 (Cq); EIMS m/z 394/392 (M^+, 19/19), 321 (100), 319

(100), 240 (45), 239 (48), 196 (31), 195 (61), 168 (52), 167 (54); HR-EIMS *m*/*z* calcd for $C_{17}H_{17}{}^{79}BrN_2O_4$ 392.0372, found 392.0381.

4.1.6. Preparation of 3,3-bis-(ethoxycarbonyl)-3,3a-dihydro-10H-[1,2,3]triazolo[1',5':1,2]-pyrrolo[3,4-b]-quinoxaline, ***1b****.* A mixture of **6** (0.41 g, 1.05 mmol) and sodium azide (0.17 g, 2.61 mmol) in 15 mL of 95% ethanol was stirred at room temperature for 12 h. The solvent was removed and the residue was treated with water (25 mL) and dichloromethane (3×10 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was column chromatographed using hexane/ethyl acetate (1:1) as eluent to give **1b** (0.34 g, 91%). As a white solid; mp 125–126 °C; R_f=0.65 (hexane/ethyl acetate=1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (t, *J*=7.2 Hz, 3H), 1.40 (t, *J*=7.2 Hz, 3H), 4.29–4.38 (m, 3H), 4.46–4.54 (m, 1H), 4.93 (d, *J*=17.4 Hz, 1H), 5.55 (d, *J*=17.4 Hz, 1H), 5.86 (s, 1H), 7.72–7.82 (m, 2H), 7.90–8.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8 (CH_3), 13.9 (CH_3), 53.8 (CH_2), 62.7 (CH_2), 63.6 (CH_2), 65.6 (CH), 95.9 (Cq), 129.2 (CH), 129.3 (CH), 130.2 (CH), 130.6 (CH), 142.0 (Cq), 142.4 (Cq), 152.4 (Cq), 153.3 (Cq), 163.6 (Cq), 164.2 (Cq); EIMS *m*/*z* 355 (M^+, 1), 255 (39), 210 (50), 209 (47), 183 (100), 181 (63), 169 (45), 142 (36), 102 (46); HR-EIMS *m*/*z* calcd for $C_{17}H_{17}N_5O_4$ 355.1281, found 355.1282.

4.2. Photolysis of 1a, 1b in CH_3CN by UV light (254nm) at room temperature

Samples **1a** and **1b** (25 mM) in CH_3CN without dienophiles were irradiated in a Rayonet photoreactor with 254 nm at room temperature for 30 min using 3 mm sealed quartz tubes, respectively. In the presence of various dienophiles (75 mM), the irradiation period is 2 h. Yields were determined using 1,4-dioxane as an internal standard and analyzed by HPLC. Because of facing difficulty in separation, we were unable to obtain a pure form of **14a** and **16a**; nevertheless, the characteristic peaks of **14a** and **16a** can be discerned from their ^{1}H and ^{13}C NMR spectra.

4.2.1. Data for diethyl 2-(2,3-dihydropyrrolo[3,4-b]quinoxalin-1-ylidene)malonate, ***9b****.* A yellow solid (5–23%); mp 182–183 °C; R_f=0.35 (hexane/ethyl acetate=1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, *J*=7.2 Hz, 3H), 1.38 (t, *J*=7.2 Hz, 3H), 4.29 (q, *J*=7.2 Hz, 2H), 4.51 (q, *J*=7.2 Hz, 2H), 4.88 (s, 2H), 7.80–7.90 (m, 2H), 8.11–8.16 (m, 2H), 9.00 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 (CH_3), 14.4 (CH_3), 29.7 (Cq), 49.3 (CH_2), 60.3 (CH_2), 61.3 (CH_2), 129.0 (CH), 130.3 (CH), 130.4 (CH), 131.5 (CH), 142.3 (Cq), 142.5 (Cq), 147.3 (Cq), 154.7 (Cq), 155.0 (Cq), 166.9 (Cq), 167.9 (Cq); EIMS *m*/*z* 327 (M^+, 26), 282 (33), 255 (43), 210 (56), 183 (100), 102 (20); HR-EIMS *m*/*z* calcd for $C_{17}H_{17}N_3O_4$ 327.1219, found 327.1210.

*4.2.2. Data for cycloadduct exo-****10b****.* A white solid (8%); mp 228–229 °C; R_f=0.38 (hexane/ethyl acetate=1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.06 (s, 1H), 3.26 (s, 2H), 5.11 (s, 2H), 7.35 (d, *J*=7.2 Hz, 2H), 7.42–7.52 (m, 3H), 7.76–7.80 (m, 2H), 8.04–8.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 46.9 (CH), 63.7 (CH), 126.5 (CH), 128.9 (CH), 129.2 (CH), 129.3 (CH), 130.0 (CH), 132.0 (Cq), 140.6 (Cq), 160.8 (Cq), 174.7 (Cq); EIMS *m*/*z* 342 (M^+, 2), 169 (100); HR-EIMS *m*/*z* calcd for $C_{20}H_{14}N_4O_2$ 342.1117, found 342.1113.

*4.2.3. Data for cycloadduct endo-****11a****.* A red solid (5%); mp 125–126 °C; R_f=0.43 (hexane/ethyl acetate=1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (t, *J*=7.2 Hz, 6H), 3.58 (s, 1H), 4.03 (dd, *J*=3.3, 1.8 Hz, 2H), 4.20–4.28 (m, 4H), 4.98 (dd, *J*=3.5, 1.8 Hz, 2H), 6.38–6.41 (m, 2H), 7.24–7.26 (m, 3H), 7.33–7.37 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9 (CH_3), 46.9 (CH), 62.1 (CH_2), 64.2 (CH), 66.6 (CH), 124.0 (CH), 126.2 (CH), 126.3 (CH), 128.5 (CH), 128.6 (CH), 128.9 (CH), 130.9 (Cq), 139.0 (Cq), 166.2 (Cq), 174.2 (Cq); EIMS *m*/*z* 448 (M^+, 2), 275 (100), 173 (47), 131 (38), 130 (60); HR-EIMS *m*/*z* calcd for $C_{25}H_{24}N_2O_6$ 448.1634, found 448.1631.

4.2.4. Data for cycloadduct ***12b****.* A yellow solid (6%); mp 172–173 °C; R_f=0.49 (hexane/ethyl acetate=1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (t, *J*=7.1 Hz, 3H), 1.26 (s, 1H), 1.40 (t, *J*=7.2 Hz, 3H), 3.32 (d, *J*=7.2 Hz, 1H), 3.75 (d, *J*=7.2 Hz, 1H), 4.15 (t, *J*=6.9 Hz, 2H), 4.41–4.49 (m, 2H), 4.46 (s,1H), 5.07 (s,1H), 7.33–7.52 (m, 5H), 7.71–7.79 (m, 2H), 8.02–8.05 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9 (CH_3), 14.1 (CH_3), 47.8 (CH), 48.3 (CH), 51.3 (CH), 61.9 (CH_2), 62.1 (CH_2), 62.4 (CH), 70.9 (Cq), 126.5 (CH), 128.9 (CH), 129.0 (CH), 129.2 (CH), 129.6 (CH), 129.7 (CH), 129.9 (CH), 131.8 (Cq), 140.3 (Cq), 140.6 (Cq), 160.1 (Cq), 160.3 (Cq), 166.6 (Cq), 168.0 (Cq), 173.9 (Cq), 174.4 (Cq); EIMS *m*/*z* 500 (M^+, 2), 327 (100), 255 (60), 254 (80), 210 (51), 209 (40), 208 (87), 127 (94), 173 (87); HR-EIMS *m*/*z* calcd for $C_{27}H_{24}N_4O_6$ 500.1696, found 500.1694.

4.2.5. Data for cycloadduct ***13a****.* A red liquid (17%); R_f=0.73 (hexane/ethyl acetate=1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (s, 1H), 3.96 (s, 6H), 7.63 (dd, *J*=6.3, 3.3 Hz, 2H), 7.93 (dd, *J*=6.3, 3.3 Hz, 2H), 8.26 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.7 (CH_3), 128.4 (Cq), 128.6 (CH), 128.7 (CH), 130.1 (CH), 133.4 (Cq), 168.2 (Cq); EIMS *m*/*z* 259 (M^+, 1), 244 (35), 213 (100); HR-EIMS *m*/*z* calcd for $C_{14}H_{13}NO_4$ 259.0845, found 259.0837.

4.2.6. Data for cycloadduct ***14a****.* A red solid (11%); mp 91–92 °C; R_f=0.48 (hexane/ethyl acetate=1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, *J*=7.2 Hz, 6H), 3.79 (s, 6H), 4.25 (q, *J*=7.2 Hz, 4H), 5.26 (s, 2H), 7.08 (dd, *J*=5.1, 3.0 Hz, 2H), 7.41 (dd, *J*=5.1, 3.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9 (CH_3), 52.3 (CH_3), 62.0 (CH_2), 64.8 (CH), 72.3 (CH), 123.3 (CH), 126.2 (CH), 144.7 (Cq), 149.4 (Cq), 163.3 (Cq), 166.2 (Cq); EIMS *m*/*z* 417 (M^+, 3), 344 (19), 312 (100), 275 (20), 224 (21), 213 (32); HR-EIMS *m*/*z* calcd for $C_{21}H_{23}NO_8$ 417.1424, found 417.1421.

4.2.7. Data for cycloadduct ***15b****.* A red solid (9%); mp 157–158 °C; R_f=0.53 (hexane/ethyl acetate=1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.17 (t, *J*=7.2 Hz, 6H), 3.72 (d, *J*=3.0 Hz, 1H), 3.90 (s, 3H), 3.96 (s, 3H), 4.18–4.25 (m, 4H), 7.81–7.86 (m, 4H), 8.12–8.14 (m, 1H), 8.18–8.19 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1 (CH_3), 52.0 (CH), 52.1 (CH_3), 52.5 (CH_3), 61.4 (CH_2), 117.0 (Cq), 129.5 (CH), 130.8 (CH), 131.8 (CH), 134.8 (Cq), 136.8 (Cq), 141.0 (Cq), 142.8 (Cq), 143.8 (Cq), 150.2 (Cq), 167.3 (Cq), 168.3 (Cq), 169.0 (Cq); EIMS *m*/*z* 469 (M^+, 100), 423 (85), 396 (49), 368 (46), 351 (32), 308 (95), 276 (45); HR-EIMS *m*/*z* calcd for $C_{23}H_{23}N_3O_8$ 469.1483, found 469.1485.

4.2.8. Data for cycloadduct ***16a****.* A white solid (3%); mp 117–119 °C; R_f=0.58 (hexane/ethyl acetate=1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19–1.27 (m, 6H), 2.65 (d, *J*=4.5 Hz, 1H), 3.63 (s, 1H), 3.70 (t, *J*=4.5 Hz, 1H), 4.05–4.20 (m, 4H), 4.93 (s, 1H), 5.05 (d, *J*=4.2, 1H), 7.35–7.49 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9 (CH_3), 35.4 (CH), 36.3 (CH), 62.0 (CH_2), 62.1 (CH_2), 63.4 (CH), 66.3 (CH), 68.4 (CH), 117.0 (Cq), 118.3 (Cq), 122.5 (CH), 124.4 (CH), 129.2 (CH), 129.2 (CH), 138.3 (Cq), 140.1 (Cq), 166.0 (Cq), 166.0 (Cq); EIMS *m*/*z* 353 (M^+, 1), 275 (100), 131 (32), 130 (64); HR-EIMS *m*/*z* calcd for $C_{19}H_{19}N_3O_4$ 353.1736, found 353.1743.

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Supplementary data

^{1}H and ^{13}C NMR spectra of compounds reported in this work and EPR spectra of the photolysis of **1a** and **1b** in MTHF at 77 K.

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2009.11.004.

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