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Efficient syntheses of 3*H*-azuleno[8,1-*cd*]pyridazines and their thermal and photochemical reactions

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ABSTRACT

Azulenopyridazines **6** were efficiently synthesized from ethyl 4-hydrazinylazulene-1-carboxylate (**2**) by *p*-toluenesulfonic acid-catalyzed imine formation and intramolecular cyclization followed by dehydrogenation using KOH/MeOH in one-pot operation. Thermal and photochemical reactions of azulenopyridazines **6** afforded 1-vinylazulenes **7** in good yields.

Azulene and substituted azulenes have attracted chemists' attention for years owing to their specific physical and chemical properties,[1] as well as the potential uses in medicine as anticancer agents,[2] antiulcer drugs,[3] antimicrobial agents,[4] antioxidant therapeutics,[5] and anti-inflammatory agents.[6] In recent years increasing interests in this type of compounds have focused on their optical, electrochemical, and physicochemical properties such as dyes,[7a] nonlinear optical,[7b,c] liquid crystals,[7d] near-infrared quenchers,[7e] and electrochromic materials.[7f] Previously few synthetic methods were reported for the syntheses of 1-vinylazulenes; most widely used methods were the Wittig reactions of 1-azulenecarbaldehydes or azulene ylides using strong bases,[7c,8a,b] the condensation of the active methylene group with Schiff bases which were generated from azulene carbaldehydes,[8c] and the condensation of the Meldrum's acid with 1-azulenecarbaldehyde.[8d]

Owing to our continuing interests related to substituted azulenes,[9] we have studied the syntheses of 3*H*-azuleno[8,1-*cd*]pyridazines (**6**) and their thermal[10] and photochemical reactions[9d,10c,11] leading to the formation of 1-vinylazulenes **7** and report herein our findings.

We have found that ethyl 4-hydrazinylazulene-1-carboxylate (**2**) was readily prepared in 80% yield from ethyl 4-ethoxyazulene-1-carboxylate (**1**)[9a] and hydrazine in refluxing ethanol for 1 h. A solution of **2** and acetone in ethanol was refluxed for 1 h afforded ethyl 4-[2-(propan-2-ylidene)hydrazinyl]azulene-1-carboxylate (**4a**) in 97% yield, which was treated with catalytic amount of *p*-toluenesulfonic acid (*p*-TSA) at reflux temperature for 1 h undergoing intramolecular Friedel–Crafts type cyclization[12] to afford dihydroazulenopyridazine **5a** in 87% yield (Scheme 1); compound **5b** was obtained in 94% yield by replacing acetone with 2-butanone (Scheme 1). The structures of the dihydroazulenopyridazines **5a** and **5b** were confirmed by ^{1}H NMR, ^{13}C NMR, IR, and MS data analyses.

In order to oxidize dihydroazulenopyridazines **5** to azulenopyridazines **6**, we found, after several attempts with various reaction conditions,[10a,13] that treatments of dihydroazulenopyridazines **5a** and **5b** with KOH/MeOH solution in an open system at room temperature for 1 h afforded the desired dehydrogenated products **6a** and **6b** in 96% and 94% yields, respectively (Table 1, entries 1 and 2). When dihydroazulenopyridazine **5a** in MeOH was treated with Br_2 at room temperature for 0.3 h, **6a** was also obtained in 88% yield (Table 1, entry 3). The structures of the azulenopyridazines **6a** and **6b** were confirmed by ^{1}H NMR, ^{13}C NMR, IR, and MS data analyses. The structure of **6a** was further unambiguously confirmed by single-crystal X-ray analysis and the ORTEP structure of **6a** is shown in Figure 1.[14]

In order to improve the efficiency of the synthetic procedure for the preparation of azulenopyridazines **6**, we decided to test one-pot reaction without purification of **5**. A solution of ethyl 4-hydrazinylazulene-1-carboxylate (**2**), acetone (**3a**), and catalytic amount of *p*-TSA was refluxed in ethanol for 1 h afforded the dihydroazulenopyridazine **5a**, which was further treated with KOH/MeOH solution in an open system at room temperature for 1 h afforded the desired dehydrogenated product **6a** in 86% yield (Table 2, entry

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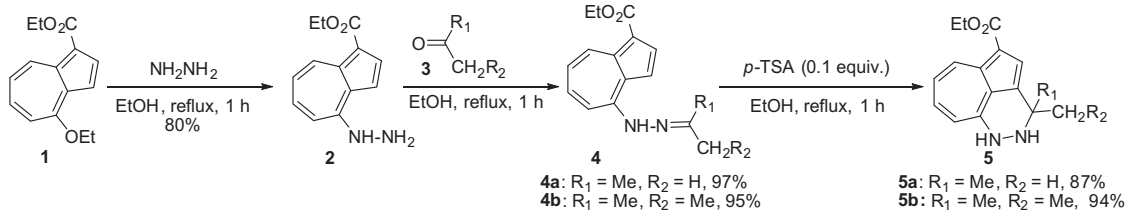
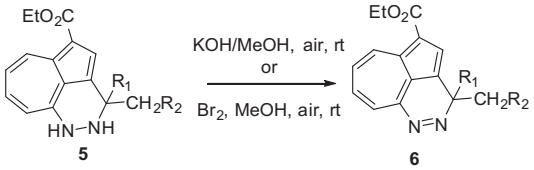


Scheme 1. Syntheses of dihydroazulenopyridazines **5a** and **5b**.

Table 1
Dehydrogenation of dihydroazulenopyridazines **5a** and **5b**



Entry	R_1	R_2	Reactant **5**	Reagent	Time (h)	Product **6** yield[a] (%)
1	Me	H	**5a**	KOH	1.0	96 **6a**
2	Me	Me	**5b**	KOH	1.0	94 **6b**
3	Me	H	**5a**	Br_2	0.3	88 **6a**

[a] Isolated yields after silica gel column chromatography.

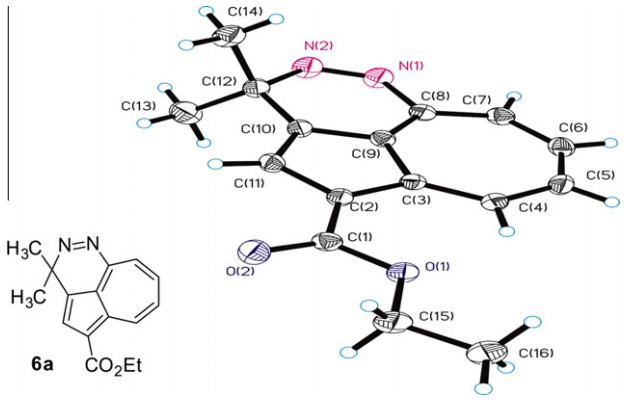
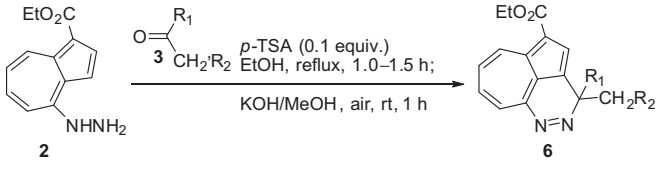


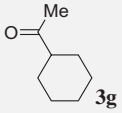
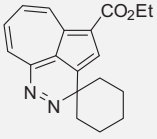
Figure 1. ORTEP diagram of ethyl 3,3-dimethyl-3*H*-azuleno[8,1-*cd*]pyridazine-5-carboxylate (**6a**).

1).[15] In order to test the compatibility of the one-pot procedure, we prepared several substituted azulenopyridazines **6b–6g** from substrates **2** and various ketones **3** in a similar procedure (Table 2, entries 2–7). 2-Butanone (**3b**), isobutyl methyl ketone (**3c**), and pentan-3-one (**3d**) gave the **6b–6d**, respectively, in excellent yields (Table 2, entries 1–4); however ethyl 3-oxobutanoate (**3e**), acetophenone (**3f**), and 1-cyclohexyl-ethanone (**3g**) produced **6e–6g** in good (66–79%) yields (Table 2, entries 5–7). These results indicate the efficiency of the imine formation, intramolecular Friedel–Crafts reaction, and dehydrogenation in one-pot operation to give **6**.

We observed that azulenopyridazine **6a**, upon refluxing in toluene for 2 h gave ethyl 3-(prop-1-en-2-yl)azulene-1-carboxylate (**7a**) in 96% yield by elimination of N_2.[16] We envisioned that **6a** might proceed via a similar reaction under photochemical conditions. Several experiments in various conditions were carried out with **6a** by changing the wavelength of the incident light, the solvents, and the irradiation time period. The best results were obtained when **6a** in acetone was irradiated with light of 350 nm region for 12 h to give **7a** in 72% yield (Table 3, entry 1).[17] In order

Table 2
One-pot method for the syntheses of azulenopyridazines **6**



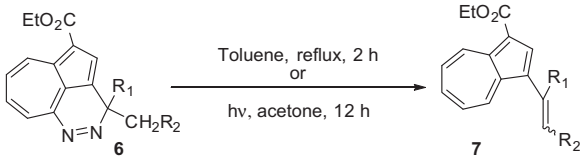
Entry	R_1	R_2	Reactant **3**	Time (h) *p*-TSA	Product **6** yield[a] (%)
1	Me	H	**3a**	1.0	86 **6a**
2	Me	Me	**3b**	1.0	80 **6b**
3	Me	$CHMe_2$	**3c**	1.2	82 **6c**
4	Et	Me	**3d**	1.2	85 **6d**
5	Me	CO_2Et	**3e**	1.5	75 **6e**
6	Ph	H	**3f**	1.0	66 **6f**
7	—	—	 **3g**	1.2	 79 **6g**

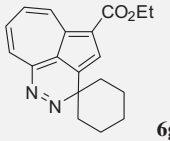
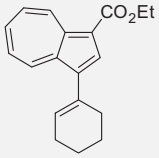
[a] Isolated yields after silica gel column chromatography.

to know the source of the newly bonded proton in the azulene ring and to have a better understanding of the plausible mechanism of the formation of product **7**, we envisioned that deuterium-labeling experiments would give the answer. We synthesized the deuterium-labeled azulenopyridazine **8** using a similar condition for **6** except that commercially available acetone-d_6 (**3a**′) was used. A dilute solution of deuterium-labeled azulenopyridazine **8** in toluene when heated at reflux for 2 h gave the deuterium-incorporated product **9** in 99% yield, whereas 65% yield of **9** was obtained in photochemical condition (Scheme 2). This result indicates that the newly bonded proton in the azulene ring of the product **7** came from the methyl or the methylene group of the reactant **6** through an intramolecular 1,5-hydrogen shift, not from the solvent or water during workup (Table 3).

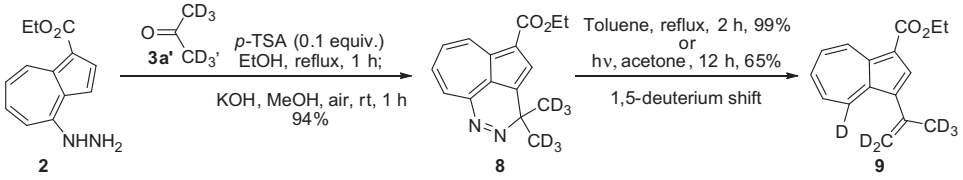
To study the scope of this transformation, various substituted substrates **6b**–**6g** were examined thermally and photochemically, and the results are summarized in Table 3. When substituents at R_1 and R_2 were methyl groups, there was a possibility of either the methylene hydrogens (CH_2R_2) or the methyl hydrogens (R_1) participating in this reaction. When heated at reflux for 2 h, **6b** produced ethyl 3-(but-2-en-2-yl)azulene-1-carboxylate (**7b**) as a mixture of diastereomers (*E*/*Z* = 0.9:1.0) in 96% yield, when irradiated with light of 350 nm region for 12 h, **6b** gave **7b** as a mixture of diastereomers in a slightly different ratio (*E*/*Z* = 1.0:0.9) in 73% yield along with ethyl 3-(but-1-en-2-yl)azulene-1-carboxylate (**7b**′) as a minor product in 14% yield (Table 3, entry 2). The formation of **7b** as a major product over **7b**′ indicates that the reaction pathway is favored via methylene hydrogen abstraction (CH_2R_2)

Table 3
The preparation of 1-vinyl azulenes **7** from 3*H*-azuleno[8,1-*cd*]pyridazines **6** in thermal and photochemical reaction conditions



Entry	R_1	R_2	Reactant **6**	Product **7** thermal conditions (Δ) Yield[a] (%)	Product **7** photochemical conditions (hν) Yield[a] (%)
1	Me	H	**6a**	96 **7a**	72 **7a**
2	Me	Me	**6b**	96 (*E*/*Z* = 0.9:1.0) **7b**	73 (*E*/*Z* = 1.0:0.9) **7b**; 14 **7b′**
3	Me	$CHMe_2$	**6c**	91 (*E*/*Z* = 1.0:0.8) **7c**; 6 **7c′**	60 (*E*/*Z* = 1.0:0.8) **7c**; 14 **7c′**
4	Et	Me	**6d**	98 (*E*/*Z* = 0.4:1.0) **7d**	73 (*E*/*Z* = 0.8:1.0) **7d**
5	Me	CO_2Et	**6e**	97 (*E*/*Z* = 0.8:1.0) **7e**	60 (*E*/*Z* = 1.0:0.9) **7e**; 18 **7e′**
6	Ph	H	**6f**	86 **7f**	74 **7f**
7	—	—	 **6g**	 98 **7g**	71 **7g**

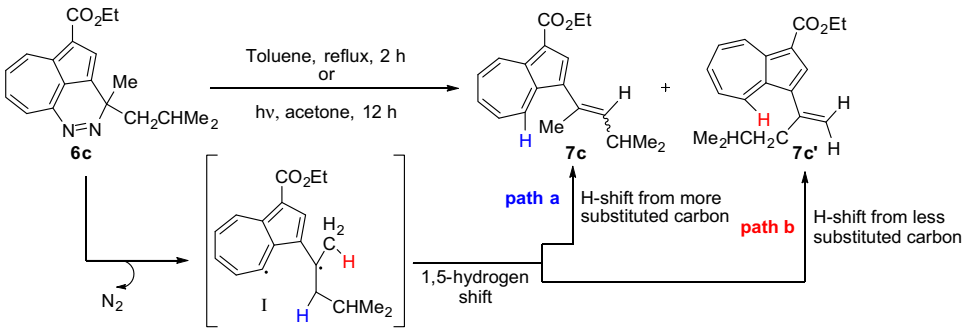
[a] Isolated yields after silica gel column chromatography; all compounds were characterized by ^1H NMR, ^{13}C NMR, IR, and MS data analyses, 14% yield of ethyl 3-(but-1-en-2-yl)azulene-1-carboxylate (**7b′**) was isolated as a minor product; 6% (Δ) and 14% (hν) yields of ethyl 3-(4-methylpent-1-en-2-yl)azulene-1-carboxylate (**7c′**) were isolated as a minor product; 18% yield of ethyl 3-(4-ethoxy-4-oxobut-1-en-2-yl)azulene-1-carboxylate (**7e′**) was isolated as a minor product; entry 6 (hν) reaction completed in 1 h.



Scheme 2. Deuterium-labeling experiment.

to form more highly substituted product double bond (Table 3, entry 2). In the case of substituents at R_1 and R_2 were methyl and an isopropyl groups respectively, **7c** was produced as a mixture of *E*/*Z* diastereomers (*E*/*Z* = 1.0:0.8) in 91% yield along with 3-(4-methylpent-1-en-2-yl)azulene-1-carboxylate (**7c′**) in 6% yield in thermal reaction, whereas 60% yield of **7c** (*E*/*Z* = 1.0:0.8) and 14% yield of **7c′** were obtained under photochemical conditions (Table 3, entry 3). Interestingly, when R_1 was an ethyl and R_2 was a methyl group, only the more substituted olefin **7d** was generated as a mixture of *E*/*Z* diastereomers in 98% (*E*/*Z* = 0.4:1.0) and 73% (*E*/*Z* = 0.8:1.0) yields under the thermal and photochemical conditions, respectively (Table 3, entry 4). Substrate **6e** containing R_2 as an ethoxycarbonyl group, when heated at reflux for 2 h, produced **7e** (*E*/*Z* = 0.8:1.0) in 97% yield (Table 3, entry 5), while, under a standard photochemical conditions, gave **7e** (*E*/*Z* = 1.0:0.9) in 60% yield along with **7e′** in 18% yield (Table 3, entry 5). Similarly, substrate **6f** (R_1 as a phenyl group) produced **7f** in 87% yield thermally and the same in 74% yield photochemically (Table 3, entry 6). Furthermore we extended the thermal and photochemical reactions to spirocyclic azulenopyridazine; thermolysis of **6g** produced **7g** in 98% yield, while irradiation (350 nm region, 12 h) of **6g** gave **7g** in 71% yield (Table 3, entry 7).

Based on the deuterium-labeling studies (Scheme 2) and the formation of products (Table 3), a plausible mechanism is proposed



Scheme 3. Plausible mechanism for the formation of 1-vinylazulenes **7c** and **7c′** from azulenopyridazine **6c** in thermal or photochemical conditions.

in Scheme 3. Azulenopyridazine **6c** decomposes under thermal or photochemical condition with elimination of N_2 to give biradical **I**, which subsequently undergoes 1,5-hydrogen shifts from the more substituted carbon (path a) or less substituted carbon (path b) via six-membered ring transition structures leading to the formation of **7c** or **7c′**, respectively.

In summary, azulenopyridazines **6**, which can be synthesized efficiently in a one-pot operation from ethyl 4-hydrazinylazulene-1-carboxylate (**2**), undergoes thermal as well as photochemical reaction with elimination of N_2 followed by a 1,5-hydrogen shift to give 1-vinylazulenes **7** in good yields.

Acknowledgments

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References and notes

1. (a) Chen, S. L.; Klein, R.; Hafner, K. *Eur. J. Org. Chem.* **1998**, 423–433; (b) Nozoe, T.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1149–1178; (c) Salman, H.; Abraham, Y.; Tal, S.; Meltzman, S.; Kapon, M.; Tessler, N.; Speiser, S.; Eichen, Y. *Eur. J. Org. Chem.* **2005**, 2207–2212.
2. (a) Asato, A. E.; Peng, A.; Hossain, M. Z.; Mirzadegan, T.; Bertram, J. S. *J. Med. Chem.* **1993**, *36*, 3137–3147; (b) Hong, B.-C.; Jiang, Y.-F.; Kumar, E. S. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 1981–1984; (c) Hidetsugu, W.; Kana, H.; Keiko, Y.; Ken, H.; Hirotaka, K.; Hirofumi, N.; Teruo, K.; Kazue, S.; Seiji, S.; Susumu, S.; Shuichi, K.; Hidecki, N.; Noboru, M.; Hiroshi, S. *Anticancer Res.* **2003**, *23*, 4747–4755.
3. Yanagisawa, T.; Wakabayashi, S.; Tomiyama, T.; Yasunami, M.; Takase, K. *Chem. Pharm. Bull.* **1988**, *36*, 641–647.
4. (a) Sullivan, B. W.; Faulkner, D. J. *J. Org. Chem.* **1986**, *51*, 5134–5136; (b) Bozin, B.; Mimica-Dukic, N.; Bogavac, M.; Suvajdzic, L.; Simin, N.; Samojlik, I.; Couladis, M. *Molecules* **2008**, *13*, 2058–2068; (c) Wang, D.-L.; Xu, J.; Han, S.; Gu, Z. *Chin. J. Org. Chem.* **2008**, *28*, 2016–2019.
5. Becker, D. A.; Ley, J. J.; Echegoyen, L.; Alvarado, R. *J. Am. Chem. Soc.* **2002**, *124*, 4678–4684.
6. Rekka, E.; Chrysselis, M.; Siskou, I.; Kourounakis, A. *Chem. Pharm. Bull.* **2002**, *50*, 904–907.
7. (a) Razus, A. C.; Birzan, L.; Nae, S.; Cristian, L.; Chiraleu, F.; Cimpeanu, V. *Dyes Pigm.* **2003**, *57*, 223–233; (b) Lacroix, P. G.; Malfant, I.; Iftime, G.; Razus, A. C.; Nakatani, K.; Delaire, J. A. *Chem. Eur. J.* **2000**, *6*, 2599–2608; (c) Iftime, G.; Lacroix, P. G.; Nakatani, K.; Razus, A. C. *Tetrahedron Lett.* **1998**, *39*, 6853–6856; (d) Estdale, S. E.; Brettle, R.; Dunmur, D. A.; Marson, C. M. *J. Mater. Chem.* **1997**, *7*, 391–401; (e) Pham, W.; Weissleder, R.; Tung, C.-H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3659–3662; (f) Ito, S.; Morita, N. *Eur. J. Org. Chem.* **2009**, 4567–4579.
8. (a) McDonald, R. N.; Stewart, W. S. *J. Org. Chem.* **1965**, *30*, 270–273; (b) Currie, J. O., Jr.; Labar, R. A.; Breazeale, R. D.; Anderson, A. G., Jr. *Justus Liebigs Ann. Chem.* **1973**, 166–180; (c) Razus, A. C.; Nitu, C.; Tecuceanu, V.; Cimpeanu, V. *Eur. J. Org. Chem.* **2003**, 4601–4610. and references cited therein; (d) Razus, A. C.; Birzan, L.; Cristian, L.; Tecuceanu, V. *ARKIVOC* **2009**, *xi*, 31–34.
9. (a) Wu, C.-P.; Cheng, L.-Y.; Wen, Y.-S.; Hsiao, C.-D. *J. Chin. Chem. Soc.* **1997**, *44*, 265–269; (b) Yang, P.-W.; Chen, J.-A.; Wakabayashi, H.; Shindo, K.; Kurihara, T.; Wu, C.-P.; Yasunami, M.; Nozoe, T. *J. Chin. Chem. Soc.* **1997**, *44*, 5–7; (c) Wu, C.-P.; Jiang, G. J.; Hung, Y.-Y.; Yang, P.-W. *J. Chin. Chem. Soc.* **1984**, *31*, 369–375; (d) Ho, T.-I.; Ku, C.-K.; Liu, R. S. H. *Tetrahedron Lett.* **2001**, *42*, 715–717.
10. (a) Dervan, P. B.; Santilli, D. S. *J. Am. Chem. Soc.* **1980**, *102*, 3863–3870; (b) Santilli, D. S.; Dervan, P. B. *J. Am. Chem. Soc.* **1979**, *101*, 3663–3664; (c) Levek, T. J.; Kiefer, E. F. *J. Am. Chem. Soc.* **1976**, *98*, 1875–1879; (d) Novák, Z.; Vincze, Z.; Czégény, Z.; Magyarfalvi, G.; Smith, D. M.; Kotschy, A. *Eur. J. Org. Chem.* **2006**, 3358–3363; (e) Simoni, D.; Rondanin, R.; Furnò, G.; Aiello, E.; Invidiata, F. P. *Tetrahedron Lett.* **2000**, *41*, 2699–2703.
11. (a) Selco, J. I.; Brooks, T.; Chang, M.; Trieu, M. T. *J. Org. Chem.* **1994**, *59*, 429–433; (b) Fox, M. A.; Lemal, D. M.; Johnson, D. W.; Hohman, J. R. *J. Org. Chem.* **1982**, *47*, 398–404; (c) Payne, A. D.; Wege, D. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1579–1580; (d) Heath, R. B.; Bush, L. C.; Feng, X.-W.; Berson, J. A.; Scaiano, J. C.; Berinsta, A. B. *J. Phys. Chem.* **1993**, *97*, 13355–13357; (e) Blay, G.; Garcia, B.; Molina, E.; Pedro, J. R. *Org. Lett.* **2005**, *7*, 3291–3294; (f) Hsu, D.-S.; Chou, Y. Y.; Tung, Y. S.; Liao, C.-C. *Chem. Eur. J.* **2010**, *16*, 3121–3131.
12. Kametani, T.; Kigasawa, K.; Hiiragi, M.; Ishimaru, H.; Uryu, T.; Haga, S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 471–472.
13. (a) Hoogesteger, F. J.; Havenith, R. W. A.; Zwikker, J. W.; Jenneskens, L. W.; Kooijman, H.; Veldman, N.; Spek, A. L. *J. Org. Chem.* **1995**, *60*, 4375–4384. and references cited therein; (b) Overberger, C. G.; O'shaughnessy, M. T.; Shalit, H. *J. Am. Chem. Soc.* **1949**, *71*, 2661–2666.
14. Crystallographic data for the structure **6a** in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 770915. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/data_request/cif).
15. General one-pot procedure for the preparation of pyperazine **6a**: To a solution of ethyl 4-hydrazinylazulene-1-carboxylate (**2**) (300 mg, 1.3 mmol) in 4 mL ethanol, acetone (110 mg, 2 mmol) and *p*-toluenesulfonic acid (23 mg, 0.1 mmol) were added and refluxed for 1 h. The reaction mixture was cooled to room temperature; 1 mL of 1% KOH/MeOH solution was added and stirred for 1 h. The reaction was quenched with distilled water and the reaction mixture was extracted with EtOAc. The organic layer was dried over $MgSO_4$, concentrated, and chromatographed on silica gel column (Hexane/EtOAc = 4:1) to give **6a** (300.6 mg, 1.12 mmol) as a yellow-green solid (mp: 127 °C) in 86% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.41–1.46 (t, J = 7.2 Hz, 3H), 1.76 (s, 6H), 4.38–4.45 (q, J = 7.2 Hz, 2H), 7.45–7.51 (t, J = 9.9 Hz, 1H), 7.89–7.96 (t, J = 9.9 Hz, 1H), 8.15 (d, J = 9.9 Hz, 1H) 8.39 (s, 1H), 9.43 (d, J = 9.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.5 (1°), 31.5 (1°), 60.1 (2°), 69.8 (4°), 116. 3 (4°), 121.1 (4°), 124.6 (4°), 128.0 (3°), 129.1 (3°), 138.0 (4°), 138.9 (3°), 139.7 (3°), 140.0 (3°), 143.5 (4°), 165.1 (4°); IR (KBr, neat) 1677, 1602, 1031 cm^{-1}; MS (ESI) relative intensity: 291 (M^++23, 100), 269 (12), 254 (15), 195 (5); MS (EI) relative intensity: 240 (M^+−28, 54), 195 (27), 167 (100), 152 (55).
16. General procedure for the preparation of 1-vinylazulene 7**a** in thermal condition: To a solution of **6a** (268 mg, 1.0 mmol) in 10 mL of toluene was refluxed for 2 h. The reaction mixture was concentrated to give the crude residue which was purified by silica gel column chromatography (Hexane/EtOAc = 8:1) to give the **7a** (230.4 mg, 0.96 mmol) as a purple color solid (mp: 44–44.5 °C) in 96% yield.
17. General procedure for the preparation of 1-vinylazulene 7**a** in photochemical condition: To a solution of **6a** (268 mg, 1.0 mmol) in 10 mL of acetone in a pyrex vessel was degassed with Argon. The solution was irradiated with 350 nm UV light in a Rayonet reactor for 12 h. The reaction mixture was concentrated to give the crude residue which was purified by silica gel column chromatography (Hexane/EtOAc = 8:1) to give the **7a** (172.8 mg, 0.72 mmol) in 72% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40–1.45 (t, J = 7.2 Hz, 3H), 2.27 (s, 3H), 4.37–4.45 (q, J = 7.2 Hz, 2H), 5.15 (s, 1H), 5.38 (s, 1H), 7.35–7.41 (t, J = 9.9 Hz, 1H), 7.43–7.49 (t, J = 9.9 Hz, 1H), 7.70–7.77 (t, J = 9.6 Hz, 1H), 8.31 (s, 1H), 8.74 (d, J = 9.6 Hz, 1H), 9.60 (d, J = 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.6 (1°), 24.8 (1°), 59.8 (2°), 114.9 (2°), 115.5 (4°), 126.6 (3°), 127.4 (3°), 131.6 (4°), 137.1 (3°), 137.8 (3°), 138.3 (3°), 139.3 (3°), 139.4 (4°), 140.0 (4°) 141.1 (4°), 165.5 (4°); IR (KBr, neat) 1687, 1042 cm^{-1}; MS (ESI) relative intensity: 263 (M^++23, 100), 241 (11), 195 (4); MS (EI) relative intensity: 240 (M^+−28, 56), 195 (26), 167 (100), 152 (56).