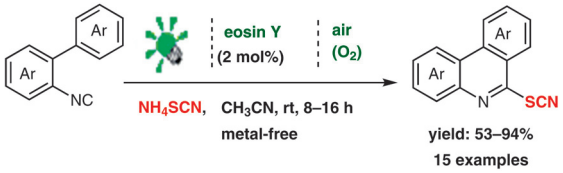
Synlett M. Singh et al. Letter

Synthesis of 6-Thiocyanatophenanthridines by Visible-Light- and Air-Promoted Radical Thiocyanation of 2-Isocyanobiphenyls

Manjula Singh[a]
Arvind K. Yadav[b]
Lal Dhar S. Yadav*[b]
R. K. P. Singh*[a]

[a] Green Synthesis Electrochemical Laboratory, Department of Chemistry, University of Allahabad, Allahabad 211002, India
[b] Green Synthesis Laboratory, Department of Chemistry, University of Allahabad, Allahabad 211002, India
ldsyadav@hotmail.com



Received: 08.08.2017
Accepted after revision: 07.09.2017
Published online: 26.09.2017
DOI: 10.1055/s-0036-1590921; Art ID: st-2017-b0602-l

Abstract A convenient, efficient, and metal-free synthesis of 6-thiocyanatophenanthridines by visible-light- and air-mediated, eosin Y-catalyzed, sequential radical cyclization and aromatization of 2-isocyanobiphenyls with ammonium thiocyanate is reported. Advantageously, the protocol utilizes inexpensive, clean, and sustainable natural resources such as visible light and atmospheric oxygen at room temperature in a one-pot procedure.

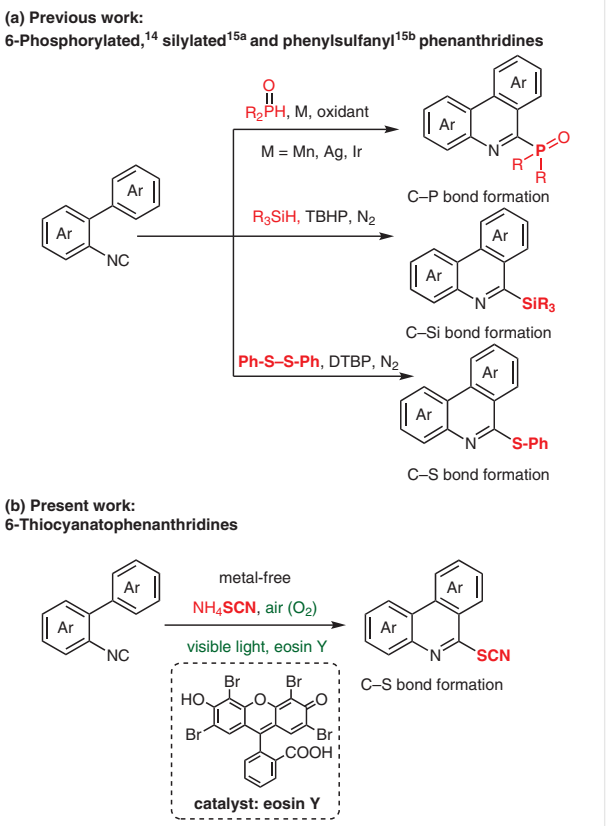
Key words radical reaction, photochemistry, cyclization, photoredox catalysis, thiocyanation, phenanthridines

Photoredox catalysis provides a great opportunity to utilize unending natural resources, such as visible light and air, in organic synthesis.[1–4] The success of this method is based on the pioneering work of the research groups of MacMillan,[1] Yoon,[2] and Stephenson,[3] who demonstrated the use of $Ru(bpy)_3Cl_2$ and $Ir(dtbbpy)_3Cl_2$ (dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) as efficient visible-light photoredox catalysts for both target-oriented and method-driven organic syntheses.[1–3] Although ruthenium and iridium complexes have proven to be efficient photoredox catalysts in numerous useful organic reactions, some organic dyes have shown promise as attractive alternatives to metal-based catalysts in visible-light-mediated photoredox reactions,[5] because they are inexpensive, easy to handle, and ecofriendly. In several cases, visible-light photoredox catalysis has utilized atmospheric oxygen to complete the catalytic cycle, and the resulting superoxide radical ($O_2^{\bullet-}$) can also act in situ as an oxidant in the synthesis.[1e,2b,3,6]

The phenanthridine ring system features in a variety of biologically active compounds and natural products.[7] Many of these, especially 6-substituted phenanthridines, show antibacterial, antifungal, antiseptic, antitumoral, antiviral, cytotoxic, or antileukemic activities.[7] Consequently, various synthetic approaches to a range of phenanthridines have been reported in the literature.[8] Recently, sequential radical insertion, cyclization, and aromatization of 2-isocyanobiphenyls employing a variety of radical precursors has emerged as an efficient and general protocol for the synthesis of 6-substituted phenanthridines. In 1995, Nanni and co-workers reported an elegant approach for the construction of 6-substituted phenanthridines by the cyclization of 2-isocyanobiphenyls using an AIBN-derived radical.[9] This stimulated extensive investigations on the cross-coupling of 2-isocyanobiphenyls with various radicals such as alkyl,[10] aryl,[11] chloroalkyl,[11a] fluoroalkyl,[12] acyl,[13] P-centered,[14] silyl,[15a] or phenylsulfanyl[15b] radicals for the synthesis of a wide range of 6-substituted phenanthridines.[16] The required radicals have been generated in various ways, for example, by using a metal catalyst, under metal-free conditions, or by visible-light photoredox catalysis with ruthenium and iridium complexes or metal-free organic dyes.

With regard to heteroatom-centered radicals, only P- and Si-centered radicals have been exploited for the synthesis of 6-phosphorylated/silylated phenanthridines from 2-isocyanobiphenyls [Scheme 1(a)].[14,15] However, the introduction of the thiocyanate functionality at the 6-position of the phenanthridine system appeared interesting, because the presence of the thiocyanate moiety generally enhances the potential of these compounds in chemical and biological applications,[17] as it is readily convertible into various sulfur-containing functional groups such as thiols,[18a] thio ethers,[18b] disulfides,[18c] or thiocarbamates.[18d] To the best of our knowledge, there is no report on the synthesis of 6-thiocyanatophenanthridines. In view of these points and our continued efforts to develop convenient synthetic protocols employing eosin Y as a visible-light photoredox catalyst,[19] we conjectured that thiocyanate radicals might be easily generated from thiocyanate anions and then coupled

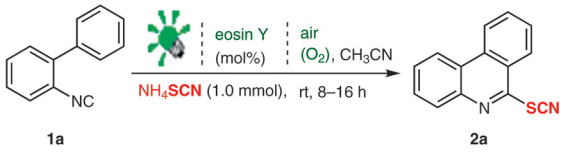
with 2-isocyanobiphenyls with subsequent cyclization and aromatization to afford 6-thiocyanatophenanthridines [Scheme1(b)].



Scheme1 Heteroatom-centered radical cyclization of 2-isocyanobiphenyls

To realize our envisaged protocol and to optimize the reaction conditions, we performed a model reaction of 2-isocyanobiphenyl (**1a**) with NH_4SCN in the presence of eosin Y as a photoredox catalyst in acetonitrile with irradiation by green light-emitting diodes (LEDs; 2.50 W, λ = 535 nm) under air at room temperature, and we were delighted to obtain the desired product **2a** in 84% yield (Table 1, entry 1). We then conducted some control experiments, which showed that the photocatalyst, air (O_2), and visible light are essential for the reaction, because in the absence of any of these, the desired product was not detected or was formed only in trace amounts (entries 3–5). The optimum amount of the eosin Y photocatalyst required for the reaction was 2 mol%. On decreasing the amount of eosin Y from 2 mol% to 1 mol%, the yield was markedly reduced (entries 1 and 6), whereas the yield was not enhanced by using 3 mol% of the photocatalyst (entries 1 and 7). The use of rose bengal (2 mol%), another organic photocatalyst, was not as effective as eosin Y (entries 1 and 2). Green LEDs (2.50 W, λ = 535 nm) were more effective than fluorescent light (entry 9), demonstrating the higher photocatalytic efficiency of eosin Y in the presence of high-intensity green light. The presence of air (O_2) is also essential for the reaction, because only a trace of product formation was observed under a nitrogen atmosphere (entry 3). Notably, the use of an oxygen balloon instead of an air atmosphere did not alter the yield (entries 1 and 10). Moreover, the reaction was quenched by TEMPO (1.0 mmol) indicating that a radical intermediate might be involved in the reaction (entry 8). We then optimized solvent and the source of thiocyanate ion. We found that CH_3CN was the best among the tested solvents (EtOH, DMF, DMSO and CH_3CN; entries 1 and 12–14) and we therefore used it throughout the remainder of our study. With regard to the thiocyanate ion source, NH_4SCN was better than KSCN in terms of the yield and time (entries 1 and 11). Blue LEDs were also tested, but these were far less effective than green LEDs (entries 1 and 15).

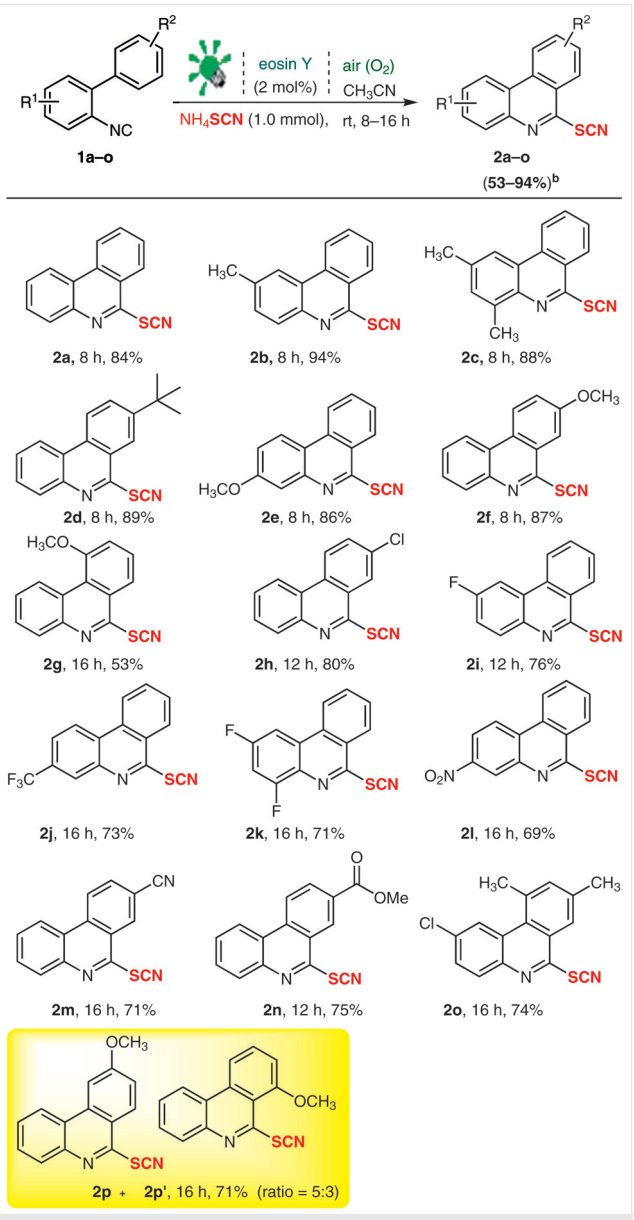
Table 1 Optimization of the Reaction Conditions[a]



Entry	Solvent	Catalyst/(mol%)	Time (h)	Yield[b] (%)
1	CH_3CN	eosin Y (2)	8	84
2	CH_3CN	rose bengal (2)	8	68
3[c]	CH_3CN	eosin Y (2)	16	traces
4[d]	CH_3CN	eosin Y (2)	16	n.d.
5[e]	CH_3CN	–	16	n.d.
6	CH_3CN	eosin Y (1)	8	67
7	CH_3CN	eosin Y (3)	8	84
8[f]	CH_3CN	eosin Y (2)	16	traces
9[g]	CH_3CN	eosin Y (2)	16	58
10[h]	CH_3CN	eosin Y (2)	16	84
11[i]	CH_3CN	eosin Y (2)	12	76
12	EtOH	eosin Y (2)	8	72
13	DMF	eosin Y (2)	8	80
14	DMSO	eosin Y (2)	8	78
15[j]	CH_3CN	eosin Y (2)	12	67

[a] Reaction conditions: **1a** (1.0 mmol), NH_4SCN (1.0 mmol), catalyst (mol%), solvent (3 mL), high-power green LEDs (Luxeon Rebel; 2.50 W, λ = 535 nm), air atmosphere, r.t.
[b] Isolated yield of the pure product **2a**.
[c] Under N_2.
[d] In darkness.
[e] The reaction was carried out in the absence of a catalyst.
[f] The reaction was quenched by TEMPO (1.0 mmol).
[g] An 18 W compact fluorescent lamp (Philips) was used.
[h] Under an O_2 balloon.
[i] KSCN was used as instead of NH_4SCN.
[j] Blue LEDs (4.45 W, λ_{max} = 447.5 nm) were used.

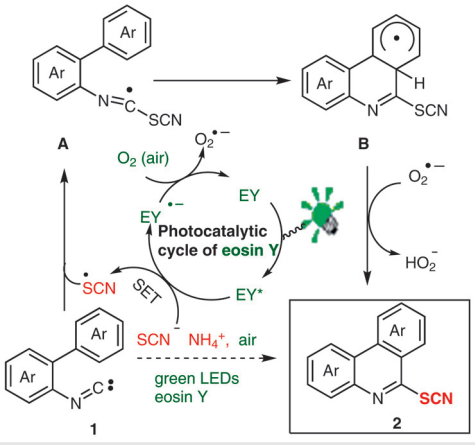
Using the optimized reaction conditions, we examined the generality and scope of the protocol across a range of 2-isocyanobiphenyls **1** incorporating various substituents, such as Me, *t*-Bu, MeO, F, Cl, CN, NO_2, and CO_2Me.[20] The reaction worked well in all the cases, affording the corresponding 6-thiocyanatophenanthridines **2** in moderate to excellent yields (Scheme 2). 2-Isocyanobiphenyls **1** bearing an electron-donating group in either aromatic ring appeared to react faster and to afford slightly higher yields of 6-thiocyanatophenanthridines compared with unsubstituted isocyanides **1** or isocyanides **1** having an electron-withdrawing group (**2b–f** versus **2a** and **2h–n**). The presence of substituents at various positions of the 2-isocyanobiphenyl **1** did not appreciably affect the yields or the reaction time, except in the case of the 2′-substituted isocyanide **1g**, which gave a significantly lower yield of **2g**, probably due to a steric effect. Moreover, the present radical cyclization reaction was also compatible with multiple substituents on the two phenyl rings of isocyanides **1** (**2c**, **2k**, and **2o**). The regioselectivity of the present cyclization was investigated with a 2-isocyanobiphenyl bearing a *m*-methoxy group, and the reaction afforded a mixture of regioisomers **2p** and **2p′** in a ratio of 5:3.



Scheme 2 Substrate scope for the synthesis of 6-thiocyanatophenanthridines **2a–o**. Yields of the pure isolated products **2** are reported.

Next, we conducted fluorescence-quenching experiments (Stern–Volmer analysis) to ascertain whether the excited eosin Y (EY*) is quenched by NH_4SCN. In the presence of NH_4SCN, the emission intensity of EY* was dramatically diminished, whereas no such effect was observed on addition of 2-isocyanobiphenyl (for details, see the Supplementary Information).

On the basis of our observations and the relevant reports in the literature,[11a,b,19d] we propose the plausible mechanistic pathway shown in Scheme 3. Eosin Y (EY), on absorption of visible light, passes into to its excited state EY*. Single-electron transfer between SCN^- and EY* affords $^{\cdot}SCN$ and $EY^{\cdot-}$. The photoredox cycle of eosin Y is completed by aerial oxidation of $EY^{\cdot-}$ to ground state EY with formation of a superoxide radical anion ($O_2^{\cdot-}$). The thiocyanate radical generated in situ attacks the 2-isocyanobiphenyl **1** to form an imidoyl radical **A**. The imidoyl radical undergoes intramolecular radical aromatic substitution to generate intermediate **B**, which is aromatized through abstraction of a hydrogen atom by $O_2^{\cdot-}$ to afford the desired 6-thiocyanato phenanthridine **2**. The formation of superoxide radical anion $O_2^{\cdot-}$ during the reaction was confirmed by detection of the resulting H_2O_2 by using KI/starch indicator.[21]



Scheme 3 A plausible mechanism for the formation of 6-thiocyanatophenanthridines **2**

In conclusion, we have developed a convenient, efficient, and metal-free synthesis of 6-thiocyanatophenanthridines by radical cyclization of 2-isocyanobiphenyls using readily available and inexpensive NH_4SCN as a source of ·SCN radicals at room temperature. The reaction involves a radical insertion/cyclization/aromatization cascade under visible-light photoredox catalysis. The salient features of the protocol include the utilization of visible light and atmospheric oxygen as sustainable, clean, and inexpensive natural resources, and eosin Y as an organophotoredox catalyst.

Acknowledgment

We sincerely thank SAIF, Punjab University, Chandigarh, for providing spectra. M.S. is grateful to the UGC, New Delhi, for a research fellowship.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1590921.

References

(1) (a) Noble, A.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2014**, *136*, 11602. (b) Terrett, J. A.; Clift, M. D.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2014**, *136*, 6858. (c) Pirnot, M. T.; Rankic, D. A.; Martin, D. B. C.; MacMillan, D. W. C. *Science* **2013**, *339*, 1593. (d) Nagib, D. A.; Scott, M. E.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2009**, *131*, 10875. (e) Nicewicz, D. A.; MacMillan, D. W. C. *Science* **2008**, *322*, 77.

(2) (a) Du, J.; Yoon, T. P. *J. Am. Chem. Soc.* **2009**, *131*, 14604. (b) Ischay, M. A.; Anzovino, M. E.; Du, J.; Yoon, T. P. *J. Am. Chem. Soc.* **2008**, *130*, 12886.

(3) (a) Konieczynska, M. D.; Dai, C.; Stephenson, C. R. J. *Org. Biomol. Chem.* **2012**, *10*, 4509. (b) Dai, C.; Narayanam, J. M. R.; Stephenson, C. R. J. *Nat. Chem.* **2011**, *3*, 140. (c) Condie, A. G.; González-Gómez, J. C.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2010**, *132*, 1464. (d) Tucker, J. W.; Narayanam, J. M. R.; Krabbe, S. W.; Stephenson, C. R. J. *Org. Lett.* **2010**, *12*, 368. (e) Narayanam, J. M. R.; Tucker, J. W.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2009**, *131*, 8756.

(4) (a) Hong, B.-C.; Kotame, P.; Tsai, C.-W.; Liao, J.-H. *Org. Lett.* **2010**, *12*, 776. (b) Zhou, J. *Chem. Asian J.* **2010**, *5*, 422. (c) Zhong, C.; Shi, X. *Eur. J. Org. Chem.* **2010**, 2999. (d) Ishikawa, H.; Suzuki, T.; Hayashi, Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 1304. (e) Jakubec, P.; Cockfield, D. M.; Dixon, D. J. *J. Am. Chem. Soc.* **2009**, *131*, 16632.

(5) For recent examples of the use of organic dyes as photoredox catalysts, see: (a) Rueping, M.; Vila, C.; Bootwicha, T. *ACS Catal.* **2013**, *3*, 1676. (b) Hari, D. P.; Schroll, P.; König, B. *J. Am. Chem. Soc.* **2012**, *134*, 2958. (c) Hari, D. P.; Hering, T.; König, B. *Org. Lett.* **2012**, *14*, 5334. (d) Hering, T.; Hari, D. P.; König, B. *J. Org. Chem.* **2012**, *77*, 10347. (e) Liu, Q.; Li, Y.-N.; Zhang, H.-H.; Chen, B.; Tung, C.-H.; Wu, L.-Z. *Chem. Eur. J.* **2012**, *18*, 620. (f) Fidaly, K.; Ceballos, C.; Falguières, A.; Veitia, M. S.-I.; Guy, A.; Ferroud, C. *Green Chem.* **2012**, *14*, 1293. (g) Yu, J.; Zhang, L.; Yan, G. *Adv. Synth. Catal.* **2012**, *354*, 2625. (h) Neumann, M.; Füldner, S.; König, B.; Zeitler, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 951. (i) Hari, D. P.; König, B. *Org. Lett.* **2011**, *13*, 3852. (j) Pan, Y.; Kee, C. W.; Chen, L.; Tan, C.-H. *Green Chem.* **2011**, *13*, 2682. (k) Pan, Y.; Wang, S.; Kee, C. W.; Dubuisson, E.; Yang, Y. K.; Loha, P.; Tan, C.-H. *Green Chem.* **2011**, *13*, 3341.

(6) (a) Yadav, A. K.; Yadav, L. D. S. *Tetrahedron Lett.* **2015**, *56*, 686. (b) Gu, L.; Jin, C.; Liu, J.; Dinga, H.; Fan, B. *Chem. Commun.* **2014**, *50*, 4643. (c) Keshari, T.; Yadav, V. K.; Srivastava, V. P.; Yadav, L. D. S. *Green Chem.* **2014**, *16*, 3986. (d) Srivastava, V. P.; Yadav, A. K.; Yadav, L. D. S. *Tetrahedron Lett.* **2014**, *55*, 1788. (e) Yadav, A. K.; Srivastava, V. P.; Yadav, L. D. S. *RSC Adv.* **2014**, *4*, 24498. (f) Xie, J.; Jin, H.; Xu, P.; Zhu, C. *Tetrahedron Lett.* **2014**, *55*, 36. (g) Nicewicz, D. A.; Nguyen, T. M. *ACS Catal.* **2014**, *4*, 355. (h) Reckenthäler, M.; Griesbeck, A. G. *Adv. Synth. Catal.* **2013**, *355*, 2727. (i) Hu, J.; Wang, J.; Nguyen, T. H.; Zheng, N. *Beilstein J. Org. Chem.* **2013**, *9*, 1977. (j) Xuan, J.; Lu, L.-Q.; Chen, J.-R.; Xiao, W.-J. *Eur. J. Org. Chem.* **2013**, 6755. (k) Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617. (l) Maity, S.; Zheng, N. *Synlett* **2012**, 1851. (m) Zou, Y.-Q.; Chen, J.-R.; Liu, X.-P.; Lu, L.-Q.; Davis, R. L.; Jørgensen, K. A.; Xiao, W.-J. *Angew. Chem. Int. Ed.* **2012**, *51*, 784.

(7) (a) Park, G. Y.; Wilson, J. J.; Song, Y.; Lippard, S. J. *Proc. Natl. Acad. Sci.* **2012**, *109*, 11987. (b) Li, K.; Frankowski, K. J.; Belon, C. A.; Neuenswander, B.; Ndjomou, J.; Hanson, A. M.; Shanahan, M. A.; Schoenen, F. J.; Blagg, B. S. J.; Aubé, J.; Frick, D. N. *J. Med. Chem.* **2012**, *55*, 3319. (c) Denny, W. A. *Curr. Med. Chem.* **2002**, *9*, 1655. (d) Ishikawa, T. *Med. Res. Rev.* **2001**, *21*, 61. (e) Nakanishi, T.; Suzuki, M.; Saimoto, A.; Kabasawa, T. *J. Nat. Prod.* **1999**, *62*, 864.

(8) (a) Tumir, L. M.; Stojković, M. R.; Piantanida, I. *Beilstein J. Org. Chem.* **2014**, *10*, 2930. (b) Walton, J. C. *Acc. Chem. Res.* **2014**, *47*, 1406. (c) Pandey, G.; Gadre, S. R. *Pure Appl. Chem.* **2012**, *84*, 1597. (d) Khadka, D. B.; Cho, W. J. *Bioorg. Med. Chem.* **2011**, *19*, 724.

(9) Nanni, D.; Pareschi, P.; Rizzoli, C.; Sgarabotto, P.; Tundo, A. *Tetrahedron* **1995**, *51*, 9045.

(10) For the synthesis of phenanthridine derivatives with alkyl radicals, see: (a) Yao, Q.; Zhou, X.; Zhang, X.; Wang, C.; Wang, P.; Li, M. *Org. Biomol. Chem.* **2017**, *15*, 957. (b) Zhou, H.; Deng, X.; Zhang, A.; Tan, R. *Org. Biomol. Chem.* **2016**, *14*, 10407. (c) Fang, H.; Zhao, J.; Ni, S.; Mei, H.; Han, J.; Pan, Y. *J. Org. Chem.* **2015**, *80*, 3151. (d) Wang, B.; Dai, Y.; Tong, W.; Gong, H. *Org. Biomol. Chem.* **2015**, *13*, 11418. (e) Xu, Z.; Yan, C.; Liu, Z.-Q. *Org. Lett.* **2014**, *16*, 5670. (f) Li, Z.; Fan, F.; Yang, J.; Liu, Z.-Q. *Org. Lett.* **2014**, *16*, 3396. (g) Zhu, Z.-Q.; Wang, T. T.; Bai, P.; Huang, Z.-Z. *Org. Biomol. Chem.* **2014**, *12*, 5839. (h) Sha, W.; Yu, J.-T.; Jiang, Y.; Yang, H.; Cheng, J. *Chem. Commun.* **2014**, *50*, 9179. (i) Wang, L.; Sha, W.; Dai, Q.; Feng, X.; Wu, W.; Chen, H. B.; Cheng, J. *Org. Lett.* **2014**, *16*, 2088. (j) Cao, J.-J.; Wang, X.; Wang, S.-Y.; Ji, S.-J. *Chem. Commun.* **2014**, *50*, 12892. (k) Yang, X.-L.; Chen, F.; Zhou, N.-N.; Yu, W.; Han, B. *Org. Lett.* **2014**, *16*, 6476. (l) Jiang, H.; Wang, Y. R.; Zheng, M.; Zhang, Y.; Yu, S. *Angew. Chem. Int. Ed.* **2013**, *52*, 13289.

(11) For the synthesis of phenanthridine derivatives with aryl radicals, see: (a) Zhou, Y.; Wu, C.; Dong, X.; Qu, J. *J. Org. Chem.* **2016**, *81*, 5202. (b) Pan, C.; Zhang, H.; Han, J.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2015**, *51*, 3786. (c) Xiao, T.; Li, L.; Lin, G.; Wang, Q.; Zhang, P.; Mao, Z.-w.; Zhou, L. *Green Chem.* **2014**, *16*, 2418. (d) Xia, Z.; Huang, J.; He, Y.; Zhao, J.; Lei, J.; Zhu, Q. *Org. Lett.* **2014**, *16*, 2546. (e) Wang, R.; Jiang, H.; Cheng, Y.; Kadi, A. A.; Fun, H.-K.; Zhang, Y.; Yu, S. *Synthesis* **2014**, 2711. (f) Tobisu, M.; Koh, K.; Furukawa, T.; Chatani, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 11363; see also Ref. 6 (b).

(12) For the synthesis of phenanthridine derivatives with chloro/fluoroalkyl radicals, see: (a) Sakamoto, R.; Kashiwagi, H.; Selvakumar, S.; Moteki, S. A.; Maruoka, K. *Org. Biomol. Chem.* **2016**, *14*, 6417. (b) Rong, J.; Deng, L.; Tan, P.; Ni, C.; Gu, Y.; Hu, J. *Angew. Chem. Int. Ed.* **2016**, *55*, 2743. (c) Wang, S.; Jia, W.-L.; Wang, L.; Liu, Q. *Eur. J. Org. Chem.* **2015**, 6817. (d) Tang, X.; Song, S.; Liu, C.; Zhu, R.; Zhang, B. *RSC Adv.* **2015**, *5*, 76363. (e) Gu, J.-W.; Zhang, X. *Org. Lett.* **2015**, *17*, 5384. (f) Zhang, Z.; Tang, X.; Dolbier, W. R. Jr. *Org. Lett.* **2015**, *17*, 4401. (g) Zhang, B.; Studer, A. *Org. Lett.* **2014**, *16*, 3990. (h) Sun, X.; Yu, S. *Org. Lett.* **2014**, *16*, 2938. (i) Zhang, B.; Mück-Lichtenfeld, C.; Daniliuc, C. G.; Studer, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 10792. (j) Wang, Q.; Dong, X.; Xiao, T.; Zhou, L. *Org. Lett.* **2013**, *15*, 4846.

(13) For the synthesis of phenanthridine derivatives with acyl radicals, see: (a) Tu, H.-Y.; Liu, Y.-R.; Chu, J.-J.; Hu, B.-L.; Zhang, X.-G. *J. Org. Chem.* **2014**, *79*, 9907. (b) Feng, X.; Zhu, H.; Wang, L.; Jiang, Y.; Cheng, J.; Yu, J.-T. *Org. Biomol. Chem.* **2014**, *12*, 9257. (c) Liu, J.; Fan, C.; Yin, H.; Qin, C.; Zhang, G.; Zhang, X.; Yi, H.; Lei, A. *Chem. Commun.* **2014**, *50*, 2145. (d) Li, X.; Fang, M.; Hu, P.; Hong, G.; Tang, Y.; Xu, X. *Adv. Synth. Catal.* **2014**, *356*, 2103. (e) Pan, C.; Han, J.; Zhang, H.; Zhu, C. *J. Org. Chem.* **2014**, *79*, 5374. (f) Leifert, D.; Daniliuc, C. G.; Studer, A. *Org. Lett.* **2013**, *15*, 6286.

(14) For the synthesis of phenanthridine derivatives with P-centered radicals, see: (a) Zhang, B.; Daniliuc, C. G.; Studer, A. *Org. Lett.* **2014**, *16*, 250. (b) Gao, Y.; Wu, J.; Xu, J.; Wang, X.; Tang, G.; Zhao, Y. *Asian J. Org. Chem.* **2014**, *3*, 691. (c) Li, Y.; Qiu, G.; Ding, Q.; Wu, J. *Tetrahedron* **2014**, *70*, 4652. (d) Cao, J.-J.; Zhu, T.-H.; Gu, Z.-Y.; Hao, W.-J.; Wang, S.-Y.; Ji, S.-J. *Tetrahedron* **2014**, *70*, 6985.

(15) For the synthesis of phenanthridine derivatives with silyl and phenylsulfanyl radicals, see: (a) Wang, L.; Zhu, H.; Guo, S.; Cheng, J.; Yu, J.-T. *Chem. Commun.* **2014**, *50*, 10864. (b) Fang, H.; Zhao, J.; Qian, P.; Han, J.; Pan, Y. *Asian J. Org. Chem.* **2014**, *3*, 1266.

(16) For reviews on the synthesis of phenanthridines through intermediate imidoyl radicals, see: (a) Lei, J.; Huang, J.; Zhu, Q. *Org. Biomol. Chem.* **2016**, *14*, 2593. (b) Yu, J.-T.; Pan, C. *Chem. Commun.* **2016**, *52*, 2220. (c) Zhang, B.; Studer, A. *Chem. Soc. Rev.* **2015**, *44*, 3505.

(17) (a) Mitra, S.; Ghosh, M.; Mishra, S.; Hajra, A. *J. Org. Chem.* **2015**, *80*, 8275. (b) Fan, W.; Yang, Q.; Xu, F.; Li, P. *J. Org. Chem.* **2014**, *79*, 10588.

(18) (a) Sengupta, D.; Basu, B. *Tetrahedron Lett.* **2013**, *54*, 2277. (b) Melzig, L.; Stemper, J.; Knochel, P. *Synthesis* **2010**, 2085. (c) Wei, Z. L.; Kozikowski, A. P. *J. Org. Chem.* **2003**, *68*, 9116. (d) Grant, M. S.; Snyder, H. R. *J. Am. Chem. Soc.* **1960**, *82*, 2742.

(19) (a) Yadav, A. K.; Yadav, L. D. S. *Green Chem.* **2016**, *18*, 4240. (b) Yadav, V. K.; Srivastava, V. P.; Yadav, L. D. S. *Tetrahedron Lett.* **2016**, *57*, 155. (c) Kapoorr, R.; Singh, S. N.; Tripathi, S.; Yadav, L. D. S. *Synlett* **2015**, *26*, 1201. (d) Yadav, A. K.; Yadav, L. D. S. *Green Chem.* **2015**, *17*, 3515. (e) Singh, A. K.; Chawla, R.; Yadav, L. D. S. *Tetrahedron Lett.* **2015**, *56*, 653. (f) Srivastava, V. P.; Yadav, A. K.; Yadav, L. D. S. *Synlett* **2014**, *25*, 665. (g) Yadav, A. K.; Yadav, L. D. S. *Tetrahedron Lett.* **2014**, *55*, 2065. (h) Yadav, A. K.; Srivastava, V. P.; Yadav, L. D. S. *RSC Adv.* **2014**, *4*, 4181.

(20) **6-Thiocyanatophenanthridines 2; General Procedure**

A mixture of the appropriate isocyanobiphenyl **1** (1 mmol), NH_4SCN **2** (1.0 mmol), eosin Y (2 mol%), and CH_3CN (3 mL) in a flask open to the air was stirred at r.t. for 8–16 h with irradiation by green LEDs (2.50 W, λ = 535 nm) (Scheme 2). When the reaction was complete (TLC), H_2O (5 mL) was added and the mixture was extracted with EtOAc (3 × 5 mL). The organic phases were combined, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting crude product was purified by chromatography [silica gel, hexane–EtOAc (4:1)].

Phenanthridin-6-yl Thiocyanate (2a)

Yellowish solid; yield: 198 mg (84%); mp 152–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (d, *J* = 8.4 Hz, 1 H), 8.63 (d, *J* = 8.4 Hz, 1 H), 8.51 (d, *J* = 8.0 Hz, 1 H), 8.22 (d, *J* = 7.6 Hz, 1 H), 7.81 (m, 1 H), 7.75–7.66 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 140.8, 134.8, 131.1, 130.6, 129.2, 129.0, 128.3, 126.6, 125.0, 122.7, 121.7, 120.6, 98.4. HRMS (EI); *m/z* calcd for $C_{14}H_8N_2S$: 236.0408; found: 236.0405.

8-Methoxyphenanthridin-6-yl Thiocyanate (2f)

Yellow solid; yield: 231 mg (87%); mp 145–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 9.2 Hz, 1 H), 8.47–8.44 (m, 1 H), 8.30 (d, *J* = 2.4 Hz, 1 H), 8.26–8.24 (m, 1 H), 7.74–7.71 (m, 2 H), 7.51 (dd, *J* = 9.2, 2.4 Hz, 1 H), 4.02 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6, 151.7, 140.0, 131.1, 129.4, 129.1, 128.2, 125.2, 124.2, 122.0, 121.5, 121.3, 109.0, 98.6, 55.7. HRMS (EI): *m/z* calcd for $C_{15}H_{10}N_2OS$: 266.0514; found: 266.0510.

8-Cyanophenanthridin-6-yl Thiocyanate (2m)

Orange solid; yield: 185 mg (71%); mp 186–189 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.25 (s, 1 H), 8.74 (d, *J* = 8.8 Hz, 1 H), 8.52 (d, *J* = 8.0 Hz, 1 H), 8.26 (d, *J* = 8.4 Hz, 1 H), 8.01 (d, *J* = 8.4 Hz, 1 H), 7.93–7.78 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0, 141.4, 137.1, 133.4, 131.7, 131.5, 131.1, 130.0, 124.0, 123.6, 122.3, 120.1, 118.2, 110.4, 97.4. HRMS (EI): *m/z* calcd for $C_{15}H_7N_3S$: 261.0361; found: 237.0364.

(21) Fekarurhobo, G. K.; Angaye, S. S.; Obomann, F. G. *J. Emerging Trends Eng. Appl. Sci.* **2013**, *4*, 394.