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1 Photosensitized, Energy-Transfer-Mediated Cyclization of 2-(1-Arylviny)benzaldehydes to Anthracen-9-(10H)-ones

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6 Supporting Information

ABSTRACT: A visible-light-induced photocatalytic intramolecular cyclization of 2-(1-arylviny)benzaldehydes is reported. The reaction is promoted in the presence of an Ir^{III} photocatalyst and an amine base at room temperature under the irradiation of blue LEDs, affording 10-methylanthracen-9(10H)-one derivatives in moderate to good yields with tolerance to various functional groups. A series of mechanistic experiments suggest that the reaction proceeds via energy transfer from the excited Ir^{III} photocatalyst to the substrate to generate a diradical, which then undergoes 1,5-hydrogen shift, 6 π electrocyclicization, and aromatization leading to the cyclic product.

Scheme 1. Photocatalytic Transformations of Alkenes via Energy Transfer

(a) Previous work

(b) Previous work

(c) This work

strong Brønsted acid or Lewis acid or preactivation of the starting materials into reactive acid halides or anhydrides.^{10–12}

We previously reported intramolecular hydroacylation of 2-(1-phenylvinyl)benzaldehyde (**1a**) promoted by a cobalt–diphosphine catalyst activated by a metallic reductant (Zn dust), affording 3-phenyl-1-indanone.¹³ The present cyclization reaction was found in our attempt to promote this hydroacylation using a photoredox catalyst and an organic reductant in place of Zn dust.¹⁴ Using the combination of

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60 Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ and *i*-Pr₂NEt, the attempted
 61 cobalt-catalyzed, visible-light-assisted hydroacylation did not
 62 yield the expected indanone product but afforded 10-
 63 methylantracen-9(10H)-one (**2a**) as the sole product (see
 64 Table S1). We then noted that the cobalt catalyst was not
 65 essential and, upon extensive optimization, managed to
 66 promote the cyclization using 5 mol % each of the Ir catalyst
 67 and the amine in DCE at room temperature under irradiation
 68 of blue LEDs, affording **2a** in 83% yield (Table 1, entry 1; see

Table 1. Effect of Reaction Conditions^a

entry	deviation from standard conditions	yield ^b (%)
1	none	81 (83) ^c
2	Ru(bpy) ₃ Cl ₂ •6H ₂ O as the photocatalyst	0
3	Ir(ppy) ₂ (dtbbpy)PF ₆ as the photocatalyst	4
4	<i>fac</i> -Ir(ppy) ₃ as the photocatalyst	38
5	Eosin Y as the photocatalyst	4
6	Et ₃ N instead of <i>i</i> -Pr ₂ NEt	58
7	pyridine instead of <i>i</i> -Pr ₂ NEt	45
8	K ₂ CO ₃ instead of <i>i</i> -Pr ₂ NEt	74
9	Cs ₂ CO ₃ instead of <i>i</i> -Pr ₂ NEt	62
10	CH ₂ Cl ₂ instead of DCE	72
11	MeCN instead of DCE	61
12	DMF instead of DCE	19
13	Ir[dF(CF ₃)ppy] ₂ (dtb-bpy)PF ₆ omitted	0
14	in the dark	0
15	<i>i</i> -Pr ₂ NEt omitted	31

^aStandard conditions: **1a** (0.1 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (0.005 mmol, 5 mol %), and *i*-Pr₂NEt (0.005 mmol, 5 mol %) in DCE (0.8 mL) at room temperature under irradiation of 7 W blue LEDs and a nitrogen atmosphere. ^bDetermined by GC using *n*-tridecane as an internal standard. ^cIsolated yield in parentheses.

69 Tables S2–S5 for more details). The reaction was found to be
 70 highly sensitive to the photocatalyst. Thus, the use of other
 71 common metal and dye photocatalysts, which possess lower
 72 triplet energies than that of Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (*E*_T
 73 = 60.8 kcal/mol),^{3b} led to significantly diminished yields or no
 74 desired product (entries 2–5). Organic and inorganic bases
 75 other than *i*-Pr₂NEt could also be used, albeit with lower
 76 reaction efficiency (entries 6–9). DCE emerged as the best
 77 solvent among others, including CH₂Cl₂, MeCN, and DMF
 78 (entries 10–12). Control experiments demonstrated that the
 79 photocatalyst and visible light are essential (entries 13 and 14).
 80 On the other hand, the reaction took place in the absence of
 81 the base albeit in a lower yield (entry 15), where the rest of the
 82 starting material was not recovered but decomposed into
 83 unidentified products.

84 With the optimized catalytic system in hand, we explored
 85 the scope of the intramolecular cyclization using various 2-(1-
 86 arylvinyl)benzaldehyde derivatives (Scheme 2). A variety of
 87 electron-withdrawing or -donating groups could be introduced
 88 to the benzaldehyde moiety, affording the corresponding
 89 products **2b–j** in moderate to good (63–84%) yields. Thus,
 90 substituents such as halogen (F, Cl), alkoxy, siloxy, alkenyl, and
 91 alkynyl groups could be well tolerated without very obvious
 92 electronic impact, while somewhat lower yield was obtained

Scheme 2. Substrate Scope^a

^aStandard conditions: **1** (0.3 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (0.015 mmol, 5 mol %), and *i*-Pr₂NEt (0.015 mmol, 5 mol %) in DCE (2.4 mL) at room temperature under irradiation of 7 W blue LEDs and a nitrogen atmosphere. ^b5 mmol scale, 48 h. ^c48 h. ^d72 h.

with the chlorinated substrate (see **2c**). The reaction of **1a** 93
 could be performed on 5 mmol scale albeit in a somewhat 94
 lower yield of 71%. 1-(1-Phenylvinyl)-2-naphthaldehyde **1k** 95
 also underwent the photocatalytic cyclization to give the 96
 desired product **2k** in 73% yield. Likewise, a variety of 97
 substituents could be introduced to the *para* position of the 98
 other aryl group of the substrate, affording the desired 99
 products **2l–t** in 63–85% yields. Note that somewhat lower 100
 yields were observed for the substrate-bearing electron- 101
 withdrawing CF₃ group (see **2v**) compared with those bearing 102
 electron-donating groups such as methoxy and alkyl groups 103
 (see **2l–o**). Interestingly, the reaction of the *p*-chloro- 104
 substituted substrate **1s** was accompanied by a benzocyclo- 105
 tanone derivative **3s** as a byproduct (18% yield). While other 106
 substrates did not give isolable and characterizable amount of 107

benzocyclobutanone byproducts, the formation of **3s** would be relevant to the mechanism of the present cyclization (vide infra). The reaction also tolerated substrates bearing 2-tolyl and 3,5-dimethylphenyl groups, affording the corresponding products **2u** and **2v** in good yields. Unfortunately, substrates bearing a heteroaryl group such as pyridine and thiophene or a β -substituent on the alkene moiety (**1w–z**) failed to produce the desired products.

To gain insight into the reaction mechanism, we performed a series of experiments. First, a light on/off experiment showed that the cyclization product **2a** formed only under irradiation of blue LEDs (Figure S2), demonstrating that the trans-formation needed continuous irradiation of visible light. Second, Stern–Volmer quenching experiments demonstrated that the olefinic substrate **1a** efficiently quenches the excited state of the Ir photocatalyst (Figure S3). The S_0 – T_1 gap for **1a** was calculated to be 53.8 kcal/mol (B3LYP/6-311+G,^{2d}p)), suggesting that the energy of the triplet state of $^*Ir^{III}$ (E_T = 60.8 kcal/mol) is sufficient for sensitizing **1a** to its triplet state. In accordance with this observation, the addition of 1 equiv of anthracene, a common triplet state quencher (E_T = 42.6 kcal/mol),^{3a,15} completely shut down the cyclization of **1a** (Scheme 3a). These facts are consistent with the hypothesis that the present reaction proceeds through a photocatalytic energy transfer pathway.

Scheme 3. Mechanistic Experiments

In order to trace the fate of the hydrogen atoms on the formyl and the *ortho* positions as well as to probe the rate-determining step, we next performed experiments using deuterium-labeled substrates. The substrate bearing a deuterated formyl group, **1a-d**, underwent cyclization with a clean transfer of the deuterium atom to the methyl position of the product **2a-d** (Scheme 3b). On the other hand, the reaction of the pentadeuterated substrate **1a-d₅** resulted in

incomplete (50%) transfer of the *ortho*-deuterium atom into the 10-position of the product (Scheme 3c). Furthermore, comparison of initial rates of parallel individual reactions of **1a** and **1a-d** gave a kinetic isotope effect (KIE) of 3.8, suggesting that the formyl C–H bond cleavage is the rate-determining step.

On the basis of the above experimental results and related literature precedents,^{3–6} we propose a reaction mechanism of the present cyclization as shown in Scheme 4. Initially,

Scheme 4. Proposed Reaction Pathway

irradiation of the Ir photocatalyst with visible light generates excited state $^*Ir^{III}$, which can sensitize the substrate **1a** via an energy-transfer process to form a triplet diradical intermediate **A**. Subsequently, 1,5-hydrogen shift of **A** gives a 1,4-diradical intermediate **B**, which would then undergo intersystem crossing and isomerization to an *o*-quinodimethane-type intermediate **C**. The formation of the benzocyclobutane byproduct **3s** may be rationalized by intramolecular radical–radical coupling of 1,4-diradical intermediate analogous to **B**. Finally, 6π electrocycloaromatization of **C** and subsequent aromatization would furnish the product **2a**. The failure of the reaction of the internal alkene substrates **1y** and **1z** might be attributed to the difficulty of 1,5-hydrogen shift of the corresponding diradical intermediates. Note that the role of the base remains unclear at this moment.

In summary, we have developed an intramolecular cyclization reaction of 2-(1-arylviny)benzaldehydes under visible-light photocatalysis, affording anthracen-9(10*H*)-one derivatives in moderate to good yields. The reaction features high atom economy, mild conditions, simple operation, and good functional group compatibility. The reaction likely involves photosensitized energy transfer as the key step, and the proposed mechanism would inspire further exploration of photocatalytic transformations of alkene-containing molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00182.

Detailed experimental procedures and characterization data for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) (a) Ravelli, D.; Dondi, D.; Fagnoni, M.; Albin, A. Photocatalysis. A multi-faceted concept for green chemistry. *Chem. Soc. Rev.* **2009**, *38*, 1999–2011. (b) Yoon, T. P.; Ischay, M. A.; Du, J. Visible light photocatalysis as a greener approach to photochemical synthesis. *Nat. Chem.* **2010**, *2*, 527–532. (c) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. Visible light photoredox catalysis with transition metal complexes: applications in organic synthesis. *Chem. Rev.* **2013**, *113*, 5322–5363. (d) Schultz, D. M.; Yoon, T. P. Solar synthesis: prospects in visible light photocatalysis. *Science* **2014**, *343*, 1239176. (e) Meggers, E. Asymmetric catalysis activated by visible light. *Chem. Commun.* **2015**, *51*, 3290–3301. (f) Wang, C.; Lu, Z. Catalytic enantioselective organic transformations via visible light photocatalysis. *Org. Chem. Front.* **2015**, *2*, 179–190. (g) Garbarino, S.; Ravelli, D.; Protti, S.; Basso, A. Photoinduced Multicomponent Reactions. *Angew. Chem., Int. Ed.* **2016**, *55*, 15476–15484. (h) Marzo, L.; Pagire, S. K.; Reiser, O.; König, B. Visible-Light Photocatalysis: Does It Make a Difference in Organic Synthesis? *Angew. Chem., Int. Ed.* **2018**, *57*, 10034–10072.
- (2) (a) Zeitler, K. Photoredox catalysis with visible light. *Angew. Chem., Int. Ed.* **2009**, *48*, 9785–9789. (b) Narayanam, J. M.; Stephenson, C. R. Visible light photoredox catalysis: applications in organic synthesis. *Chem. Soc. Rev.* **2011**, *40*, 102–113. (c) Shi, L.; Xia, W. Photoredox functionalization of C-H bonds adjacent to a nitrogen atom. *Chem. Soc. Rev.* **2012**, *41*, 7687–7697. (d) Xuan, J.; Xiao, W.-J. Visible-light photoredox catalysis. *Angew. Chem., Int. Ed.* **2012**, *51*, 6828–6838. (e) Xi, Y.; Yi, H.; Lei, A. Synthetic applications of photoredox catalysis with visible light. *Org. Biomol. Chem.* **2013**, *11*, 2387–2403. (f) Angnes, R. A.; Li, Z.; Correia, C. R.; Hammond, G. B. Recent synthetic additions to the visible light photoredox catalysis toolbox. *Org. Biomol. Chem.* **2015**, *13*, 9152–9167. (g) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075–10166. (h) Luo, K.; Yang, W.-C.; Wu, L. Photoredox Catalysis in Organophosphorus Chemistry. *Asian J. Org. Chem.* **2017**, *6*, 350–367.
- (3) (a) Strieth-Kalthoff, F.; James, M. J.; Teders, M.; Pitzer, L.; Glorius, F. Energy transfer catalysis mediated by visible light: principles, applications, directions. *Chem. Soc. Rev.* **2018**, *47*, 7190–7202. (b) Zhou, Q.-Q.; Zou, Y.-Q.; Lu, L.-Q.; Xiao, W.-J. Visible-Light-Induced Organic Photochemical Reactions via Energy Transfer Pathways. *Angew. Chem., Int. Ed.* **2019**, *58*, 1586.
- (4) For selected examples, see: (a) Farney, E. P.; Yoon, T. P. Visible-light sensitization of vinyl azides by transition-metal photocatalysis. *Angew. Chem., Int. Ed.* **2014**, *53*, 793–797. (b) Xia, X.-D.; Xuan, J.; Wang, Q.; Lu, L.-Q.; Chen, J.-R.; Xiao, W.-J. Synthesis of 2-Substituted Indoles through Visible Light-Induced Photocatalytic Cyclizations of Styryl Azides. *Adv. Synth. Catal.* **2014**, *356*, 2807–2812. (c) Brachet, E.; Ghosh, I.; König, B. Visible light C–H amidation of heteroarenes with benzoyl azides. *Chem. Sci.* **2015**, *6*, 987–992. (d) Heitz, D. R.; Tellis, J. C.; Molander, G. A. Photochemical Nickel-Catalyzed C–H Arylation: Synthetic Scope and Mechanistic Investigations. *J. Am. Chem. Soc.* **2016**, *138*, 12715–12718. (e) Scholz, S. O.; Farney, E. P.; Kim, S.; Bates, D. M.; Yoon, T. P. Spin-Selective Generation of Triplet Nitrenes: Olefin Aziridination through Visible-Light Photosensitization of Azidoformates. *Angew. Chem., Int. Ed.* **2016**, *55*, 2239–2242. (f) Bagal, D. B.; Park, S. W.; Song, H. J.; Chang, S. Visible light sensitization of benzoyl azides: cascade cyclization toward oxindoles via a non-nitrene pathway. *Chem. Commun.* **2017**, *53*, 8798–8801. (g) Luis-Barrera, J.; Laina-Martin, V.; Rigotti, T.; Peccati, F.; Solans-Monfort, X.; Sodupe, M.; Mas-Balleste, R.; Liras, M.; Aleman, J. Visible-Light Photocatalytic Intramolecular Cyclopropane Ring Expansion. *Angew. Chem., Int. Ed.* **2017**, *56*, 7826–7830. (h) Welin, E. R.; Le, C.; Arias-Rotondo, D. M.; McCusker, J. K.; MacMillan, D. W. Photosensitized, energy transfer-mediated organometallic catalysis through electronically excited nickel(II). *Science* **2017**, *355*, 380–385. (i) Zhu, S.; Pathigool, A.; Lowe, G.; Walsh, D. A.; Cooper, M.; Lewis, W.; Lam, H. W. Sulfonylative and Azidosulfonylative Cyclizations by Visible-Light-Photosensitization of Sulfonyl Azides in THF. *Chem. - Eur. J.* **2017**, *23*, 17598–17604. (j) Teders, M.; Henkel, C.; Anhauser, L.; Strieth-Kalthoff, F.; Gomez-Suarez, A.; Kleinmans, R.; Kahnt, A.; Rentmeister, A.; Guldi, D.; Glorius, F. The energy-transfer-enabled biocompatible disulfide-ene reaction. *Nat. Chem.* **2018**, *10*, 981–988. (k) Zhang, Y.; Liu, H.; Tang, L.; Tang, H. J.; Wang, L.; Zhu, C.; Feng, C. Intermolecular Carboamination of Unactivated Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 10695–10699.
- (5) (a) Lu, Z.; Yoon, T. P. Visible light photocatalysis of [2 + 2] styrene cycloadditions by energy transfer. *Angew. Chem., Int. Ed.* **2012**, *51*, 10329–10332. (b) Zou, Y.-Q.; Duan, S.-W.; Meng, X.-G.; Hu, X.-Q.; Gao, S.; Chen, J.-R.; Xiao, W.-J. Visible light induced intermolecular [2 + 2]-cycloaddition reactions of 3-ylideneoxindoles through energy transfer pathway. *Tetrahedron* **2012**, *68*, 6914–6919. (c) Alonso, R.; Bach, T. A Chiral Thioxanthone as an Organocatalyst for Enantioselective [2 + 2] Photocycloaddition Reactions Induced by Visible Light. *Angew. Chem.* **2014**, *126*, 4457–4460. (d) Hurtley, A. E.; Lu, Z.; Yoon, T. P. [2 + 2] cycloaddition of 1,3-dienes by visible light photocatalysis. *Angew. Chem., Int. Ed.* **2014**, *53*, 8991–8994. (e) Blum, T. R.; Miller, Z. D.; Bates, D. M.; Guzei, I. A.; Yoon, T. P. Enantioselective photochemistry through Lewis acid-catalyzed triplet energy transfer. *Science* **2016**, *354*, 1391–1395. (f) Lei, T.; Zhou, C.; Huang, M. Y.; Zhao, L. M.; Yang, B.; Ye, C.; Xiao, H.; Meng, Q. Y.; Ramamurthy, V.; Tung, C. H.; Wu, L. Z. General and Efficient Intermolecular [2 + 2] Photodimerization of Chalcones and Cinnamic Acid Derivatives in Solution through Visible-Light Catalysis. *Angew. Chem., Int. Ed.* **2017**, *56*, 15407–15410. (g) Pagire, S. K.; Hossain, A.; Traub, L.; Kerres, S.; Reiser, O. Photosensitized regioselective [2 + 2]-cycloaddition of cinnamates and related alkenes. *Chem. Commun.* **2017**, *53*, 12072–12075. (h) Skubi, K. L.; Kidd, J. B.; Jung, H.; Guzei, I. A.; Baik, M. H.; Yoon, T. P. Enantioselective Excited-State Photoreactions Controlled by a Chiral Hydrogen-Bonding Iridium Sensitizer. *J. Am. Chem. Soc.* **2017**, *139*, 17186–17192. (i) Wang, C.; Lu, Z. Intermolecular [2 + 2] Cycloaddition of 1,4-Dihydropyridines with Olefins via Energy Transfer. *Org. Lett.* **2017**, *19*, 5888–5891. (j) Zhao, J.; Brosmer, J. L.; Tang, Q.; Yang, Z.; Houk, K. N.; Diaconescu, P. L.; Kwon, O. Intramolecular Crossed [2 + 2] Photocycloaddition through Visible Light-Induced Energy Transfer. *J. Am. Chem. Soc.* **2017**, *139*, 9807–9810. (k) Hörmann, F. M.; Chung, T. S.; Rodriguez, E.; Jakob, M.; Bach, T. *Angew. Chem., Int. Ed.* **2018**, *57*, 827–831.
- (6) (a) Singh, K.; Staig, S. J.; Weaver, J. D. Facile Synthesis of Z-Alkenes via Uphill Catalysis. *J. Am. Chem. Soc.* **2014**, *136*, 5275–5278. (b) Metternich, J. B.; Gilmour, R. A Bio-Inspired, Catalytic E → Z Isomerization of Activated Olefins. *J. Am. Chem. Soc.* **2015**, *137*, 11254–11257. (c) Metternich, J. B.; Gilmour, R. One Photocatalyst, n Activation Modes Strategy for Cascade Catalysis: Emulating Coumarin Biosynthesis with (–)-Riboflavin. *J. Am. Chem. Soc.* **2016**, *138*, 1040–1045. (d) Metternich, J. B.; Artiukhin, D. G.; Holland, M. C.; von Bremen-Kühne, M.; Neugebauer, J.; Gilmour, R. Photocatalytic E → Z Isomerization of Polarized Alkenes Inspired by the Visual Cycle: Mechanistic Dichotomy and Origin of Selectivity. *J. Org. Chem.* **2017**, *82*, 9955–9977. (e) Fassbender, S. I.; Metternich, J. B.; Gilmour, R. Spatiotemporal Control of Pre-existing Alkene Geometry: A Bio-Inspired Route to 4-Trifluoromethyl-2H-chro-

- 314 menes. *Org. Lett.* **2018**, *20*, 724–727. (f) Metternich, J. B.; Sagebiel,
315 S.; Luckener, A.; Lamping, S.; Ravoo, B. J.; Gilmour, R. Covalent
316 Immobilization of (–)-Riboflavin on Polymer Functionalized Silica
317 Particles: Application in the Photocatalytic E→Z Isomerization of
318 Polarized Alkenes. *Chem. - Eur. J.* **2018**, *24*, 4228–4233. (g) Molloy, J.
319 J.; Metternich, J. B.; Daniliuc, C. G.; Watson, A. J. B.; Gilmour, R.
320 Contra-Thermodynamic, Photocatalytic E→Z Isomerization of
321 Styrenyl Boron Species: Vectors to Facilitate Exploration of Two-
322 Dimensional Chemical Space. *Angew. Chem., Int. Ed.* **2018**, *57*, 3168–
323 3172. (h) Singh, K.; Fennell, C. J.; Coutias, E. A.; Latifi, R.; Hartson,
324 S.; Weaver, J. D. Light Harvesting for Rapid and Selective Reactions:
325 Click Chemistry with Strain-Loadable Alkenes. *Chem.* **2018**, *4*, 124–
326 137. (i) Day, J. I.; Singh, K.; Trinh, W.; Weaver, J. D. Visible Light
327 Mediated Generation of *trans*-Arylcyclohexenes and Their Utilization
328 in the Synthesis of Cyclic Bridged Ethers. *J. Am. Chem. Soc.* **2018**, *140*,
329 9934–9941.
- 330 (7) Münster, N.; Parker, N. A.; van Dijk, L.; Paton, R. S.; Smith, M.
331 D. Visible Light Photocatalysis of 6pi Heterocyclization. *Angew.*
332 *Chem., Int. Ed.* **2017**, *56*, 9468–9472.
- 333 (8) (a) Muller, K. Antipsoriatic anthrones: aspects of oxygen radical
334 formation, challenges and prospects. *Gen. Pharmacol.* **1996**, *27*, 1325–
335 1335. (b) Koyama, Y.; Yamaguchi, R.; Suzuki, K. Total synthesis and
336 structure assignment of the anthrone C-glycoside cassialoin. *Angew.*
337 *Chem., Int. Ed.* **2008**, *47*, 1084–1087. (c) Malik, E. M.; Muller, C. E.
338 Anthraquinones As Pharmacological Tools and Drugs. *Med. Res. Rev.*
339 **2016**, *36*, 705–748. (d) Nicolaou, K. C.; Liu, G.; Beabout, K.;
340 McCurry, M. D.; Shamoo, Y. Asymmetric Alkylation of Anthrones,
341 Enantioselective Total Synthesis of (–)- and (+)-Viridicatumtoxins B
342 and Analogues Thereof: Absolute Configuration and Potent
343 Antibacterial Agents. *J. Am. Chem. Soc.* **2017**, *139*, 3736–3746.
- 344 (e) Peixoto, D.; Figueiredo, M.; Malta, G.; Roma-Rodrigues, C.;
345 Baptista, P. V.; Fernandes, A. R.; Barroso, S.; Carvalho, A. L.; Afonso,
346 C. A. M.; Ferreira, L. M.; Branco, P. S. Synthesis, Cytotoxicity
347 Evaluation in Human Cell Lines and in Vitro DNA Interaction of a
348 Hetero-Arylidene-9(10H)-Anthrone. *Eur. J. Org. Chem.* **2018**, *2018*,
349 545–549.
- 350 (9) (a) Netka, J.; Crump, S. L.; Rickborn, B. Isobenzofuran-Aryne
351 Cycloadducts - Formation and Regioselective Conversion to
352 Anthrones and Substituted Polycyclic Aromatics. *J. Org. Chem.*
353 **1986**, *51*, 1189–1199. (b) Hirakawa, K.; Ogiue, E.; Motoyoshiya, J.;
354 Kakurai, T. Preparations and Reactions of 10-(Halomethylene)-
355 Anthrones. *J. Org. Chem.* **1986**, *51*, 1083–1087. (c) Li, B.; Fan, D.;
356 Yang, C.; Xia, W. UV light-mediated difunctionalization of alkenes
357 with CF₃SO₂Na: synthesis of trifluoromethyl phenanthrene and
358 anthrone derivatives. *Org. Biomol. Chem.* **2016**, *14*, 5293–5297.
- 359 (d) Link, A.; Fischer, C.; Sparr, C. A 1,5-Bifunctional Organo-
360 magnesium Reagent for the Synthesis of Disubstituted Anthracenes
361 and Anthrones. *Synthesis* **2016**, *49*, 397.
- 362 (10) (a) Friedel, C.; Crafts, J. M. *Compt. Rend.* **1877**, *84*, 1450–
363 1454. (b) Gore, P. H. The Friedel-Crafts Acylation Reaction and Its
364 Application to Polycyclic Aromatic Hydrocarbons. *Chem. Rev.* **1955**,
365 *55*, 229–281.
- 366 (11) (a) Olah, G. A.; Mathew, T.; Farnia, M.; Prakash, G. K. S.
367 Nafion-H catalysed intramolecular Friedel-Crafts acylation: Forma-
368 tion of cyclic ketones and related heterocycles. *Synlett* **1999**, *1999*,
369 1067–1068. (b) El-Sayrafi, S.; Rayyan, S. Intramolecular acylation of
370 aryl- and aroyl-aliphatic acids by the action of pyrophosphoryl
371 chloride and phosphorus oxychloride. *Molecules* **2001**, *6*, 279–286.
372 (c) Prakash, G. K.; Mathew, T.; Marinez, E. R.; Esteves, P. M.; Rasul,
373 G.; Olah, G. A. BF₃·2CF₃CH₂OH (BF₃•2TFE), an efficient
374 superacidic catalyst for some organic synthetic transformations. *J.*
375 *Org. Chem.* **2006**, *71*, 3952–3958. (d) Lan, K.; Fen, S.; Shan, Z. X.
376 Synthesis of aromatic cycloketones via intramolecular Friedel-Crafts
377 acylation catalyzed by heteropoly acids. *Aust. J. Chem.* **2007**, *60*, 80–
378 82.
- 379 (12) (a) Fillion, E.; Fishlock, D.; Wilsily, A.; Goll, J. M. Meldrum's
380 acids as acylating agents in the catalytic intramolecular Friedel-Crafts
381 reaction. *J. Org. Chem.* **2005**, *70*, 1316–1327. (b) Song, S.; Zhu, S. F.;
382 Yu, Y. B.; Zhou, Q. L. Carboxy-directed asymmetric hydrogenation of
1,1-diarylethenes and 1,1-dialkylethenes. *Angew. Chem., Int. Ed.* **2013**, *52*, 1556–1559. (c) Motiwala, H. F.; Vekariya, R. H.; Aube, J. Intramolecular Friedel-Crafts Acylation Reaction Promoted by 1,1,1,3,3,3-Hexafluoro-2-propanol. *Org. Lett.* **2015**, *17*, 5484–5487. (13) (a) Yang, J.; Yoshikai, N. Cobalt-Catalyzed Enantioselective Intramolecular Hydroacylation of Ketones and Olefins. *J. Am. Chem. Soc.* **2014**, *136*, 16748–16751. (b) Yang, J.; Rérat, A.; Lim, Y. J.; Gosmini, C.; Yoshikai, N. Cobalt-Catalyzed Enantio- and Diastereoselective Intramolecular Hydroacylation of Trisubstituted Alkenes. *Angew. Chem., Int. Ed.* **2017**, *56*, 2449–2453. (14) Ruhl, K. E.; Rovis, T. Visible Light-Gated Cobalt Catalysis for a Spatially and Temporally Resolved [2 + 2+2] Cycloaddition. *J. Am. Chem. Soc.* **2016**, *138*, 15527–15530. (15) Zhang, Y.; Dong, X.; Wu, Y.; Li, G.; Lu, H. Visible-Light-Induced Intramolecular C(sp²)-H Amination and Aziridination of Azidoformates via a Triplet Nitrene Pathway. *Org. Lett.* **2018**, *20*, 4838–4842.