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Synthesis of 2,3-Dihydro-4-Pyridones, 4-Quinolones and 2,3-Dihydro-4-Azocinones by Visible-Light Photocatalytic Aerobic Dehydrogenation

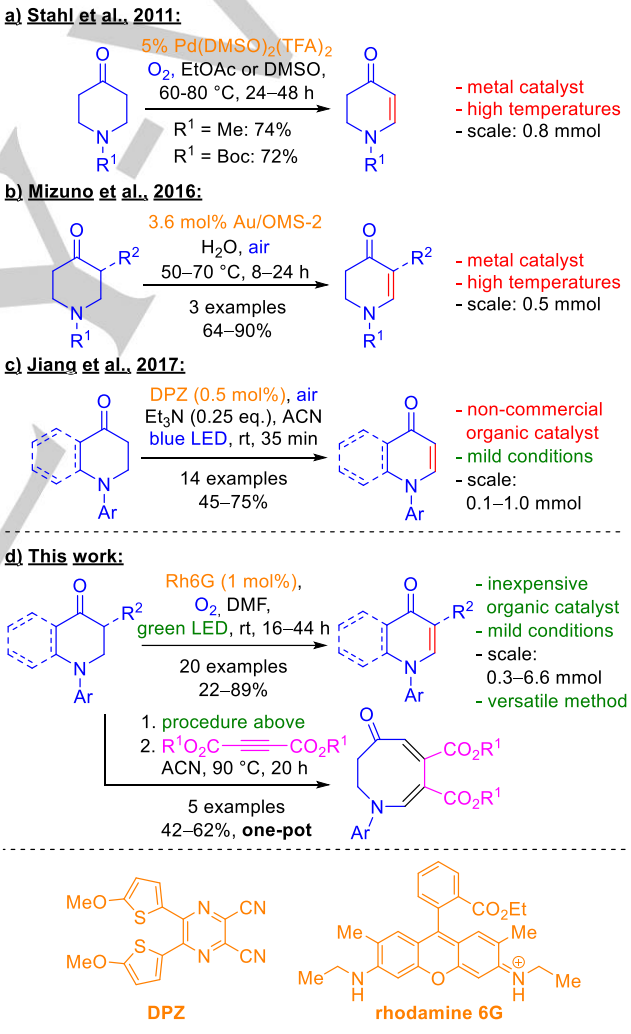
Adrian Sevenich,[a] Paulina Sophie Mark,[a] Torsten Behrendt,[a] Jonathan Groß,[a] and Till Opatz*[a]

Abstract: The synthesis of 2,3-dihydro-4-pyridones and 4-quinolones was realized by visible-light mediated photoredox-catalyzed aerobic dehydrogenation of 4-piperidones and 2,3-dihydro-4-quinolones. This method enables the synthesis of cyclic enaminones in up to 89% yield under mild and eco-friendly conditions and with a high tolerance of functional groups using oxygen as an inexpensive terminal oxidant and rhodamine 6G as a readily available organic photocatalyst. The process can be extended to access 2,3-dihydro-4-azocinones in up to 62% yield via a [2+2] cycloaddition/ring-expansion sequence in a telescoping one-pot reaction. Hence, a protocol for the synthesis of three different types of N-heterocycles was developed on the same general transformation.

Introduction

Due to the vinylogous transposition of the reactivity of the amine nitrogen and the carbonyl group, enaminones show a versatile reactivity pattern.[1] Their simple cyclic representatives such as 2,3-dihydro-4-pyridines are attractive building blocks and can e.g. be used as precursors for piperidine-based target molecules.[2] Consequently, they have been applied as building blocks for drugs[3] or for alkaloid natural products such as indolizidines and quinolizidines.[1a, 2a, 2c, 4] In addition, they represent key structures in drug candidates like peptidomimetic opioids,[5] flavivirus inhibitors[6] and antibacterial oxazolidinones.[7] Their benzo-fused relatives, the 4-quinolones, are one of the largest class of antimicrobial agents[8] and have recently attracted further attention due to their antitumor and anti-HIV activity.[8b, 8c, 9]

Dehydrogenation has been used as a direct strategy to access cyclic enaminones, since preformed heterocycles can serve as the starting materials.[2c, 3c, 10] To this end, multistep procedures based on the Polonovski reaction[10a, 10d, 10g] or the Saegusa oxidation[7a, 10m] have been used extensively. Among the one-step procedures, $Hg(OAc)_2$[10b, 10f, 10k] and DDQ[10e, 10i, 10n] have been applied by various groups. Nicolaou et al. found complexes of IBX and various amine-*N*-oxides to enable the reaction under mild condition.[10h, 10j, 10r] However, these procedures generally suffer from lengthy sequences, the use of expensive or ecologically problematic reagents or catalysts and, most notably, stoichiometric amounts of oxidants being required to effect the dehydrogenation. First achievements to replace stoichiometric reagents by oxygen as terminal oxidant have been reported by



Scheme 1. Overview of catalytic one-step syntheses of cyclic enaminones by aerobic dehydrogenation.

Stahl et al. who proposed a $Pd(DMSO)_2(TFA)_2$ catalyst which enables the dehydrogenation of cyclic ketones (Scheme 1).[10l] The group of Mizuno found a heterogeneous catalyst system consisting of gold nanoparticles supported on manganese oxide

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to perform the aerobic dehydrogenation of β-heteroatom-substituted ketones.[10p] Recently, a photoredox catalyzed approach was reported by Jiang et al. using the non-commercial dicyanopyrazine chromophore (DPZ) as a photocatalyst in combination with oxygen to obtain 2,3-dihydro-4-pyridones and 4-quinolones on a limited scale.[10o]

Photoredox catalysis through organic dyes has proven to be a valuable and often eco-friendly tool for performing a large variety of selective transformations on amines under mild conditions,[11] which were also investigated in our labs.[12] It was therefore attempted to overcome the drawbacks of above-mentioned protocols for the synthesis of cyclic enaminones using an inexpensive commercially available organic dye as catalyst and oxygen as sustainable oxidant.

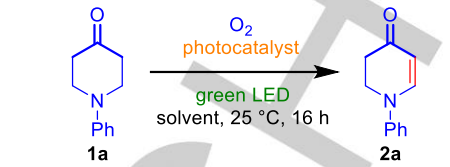
Partially saturated azocines have recently attracted attention due to their occurrence in natural products such as the manzamine alkaloids[13] and their various biological activities,[13a, 14] for example against leishmaniasis.[13a] To access this interesting group of eight-membered *N*-heterocycles, ring-expansion has become a common strategy which can e.g. be initiated by [2+2] cycloaddition of acetylene esters and cyclic enamine containing structures.[14a, 15] In this context, it appeared possible to combine the photocatalytic dehydrogenation step with a subsequent light-independent reaction like a [2+2] cycloaddition ultimately leading to ring-expansion. This would provide a direct access to eight-membered *N*-heterocycles from a completely saturated six-membered nitrogen containing precursor *via* the intermediate enaminone.

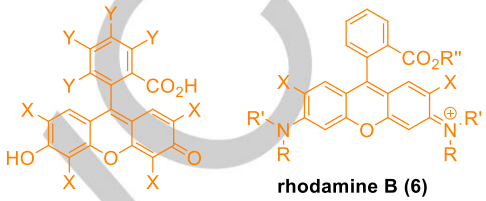
Here, we describe the synthesis of cyclic enaminones like 2,3-dihydro-4-pyridones and 4-quinolones by visible light mediated aerobic dehydrogenation and exploited their reactivity to provide access to another class of *N*-heterocycles, namely 2,3-dihydro-4-azocinones in a one-pot reaction.

Results and Discussion

We started our optimization studies in terms of reaction yield by evaluating various xanthene dyes which have commonly been used for amine oxidations.[11b, 11h, 12a] Interestingly, the most frequently used catalysts rose bengal (RB, **5**) and eosin Y (EY, **4**) gave no clean reactions (Table 1, entries 2 and 3). Although the starting material was consumed very rapidly, the product yield remained always moderate, at both low and high conversion, indicating that **2** might not be stable under these conditions. Indeed, the C=C bond cleavage of enamines and enaminones under visible light catalyzed aerobic conditions using RB and EY is well documented.[16] Even though there have been debates as to whether or not singlet oxygen is involved in this reaction,[16c] it is obvious that these conditions are not suitable and overcoming this issue would be a key challenge for the outlined approach. The low yields of **2** observed using RB and EY are in agreement with the observations by Jiang and may have prompted them to use a non-commercial dye.[10o] Gratifyingly, fluorescein (**3**) and rhodamine 6G (**7**) gave the product **2** in satisfactory yields, with **7** being slightly superior (entry 5). Further evaluation of different solvents (entries 6 to 11) revealed DMF to be the best choice.

Table 1. Optimization studies for the photocatalytic dehydrogenation.[a]





fluoresceine (3) (X,Y=H)
eosin Y (4) (X=Br, Y=H)
rose bengal (5) (X=I, Y=Cl)

rhodamine B (6)
(X,R''=H, R,R'=Et)
rhodamine 6G (7)
(X=Me, R'=H, R,R''=Et)

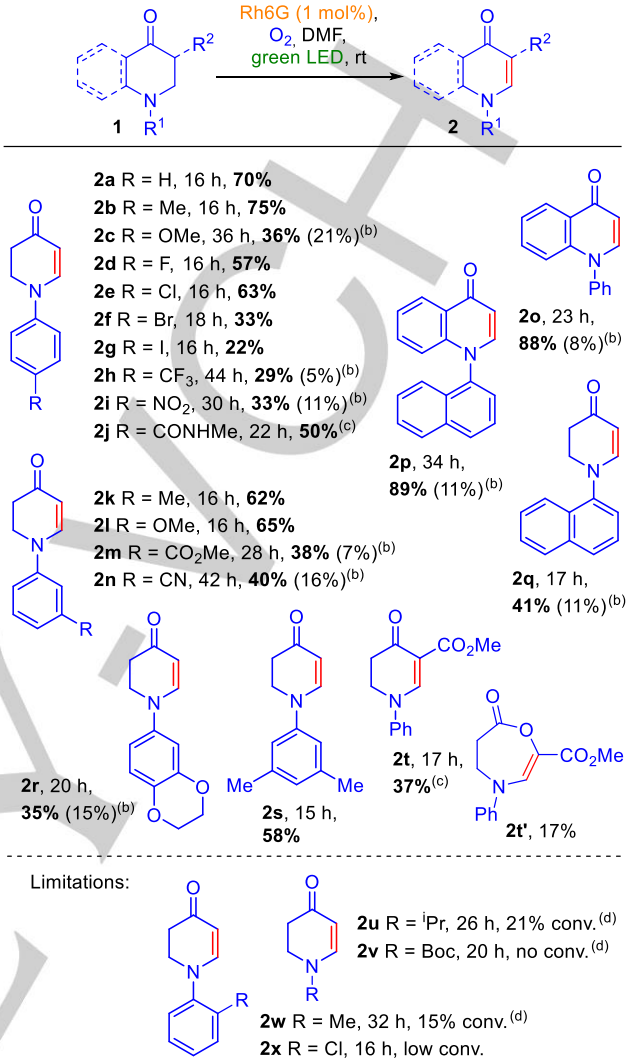
Entry	Cat. (mol%)	Solvent	1a (%)[b]	2a (%)[b]
1	**3** (5)	DMF	<1	58[c]
2	**5** (5)	DMF	<1	36
3	**4** (5)	DMF	<1	49
4	**6** (5)	DMF	13	53
5	**7** (5)	DMF	15	61
6	**7** (5)	DMSO	58	21
7	**7** (5)	MeOH	96	2
8	**7** (5)	DCM	42	35
9	**7** (5)	PhMe	85	9
10	**7** (5)	ACN	37	42
11	**7** (5)	THF	15	49
12	**7** (5)	DMF	65	24[d]
13	**7** (10)	DMF	29	47
14	**7** (2)	DMF	10	66
15	**7** (1.5)	DMF	<1	72
16	**7** (1)	DMF	<1	77 (70)[e]
17	**7** (0.5)	DMF	4	68
18	**7** (0.1)	DMF	7	59
19	-	DMF	96	0
20	**7** (1)	DMF	98	0[f]
21	**7** (1)	DMF	96	0[g]

[a]Reaction conditions: **1a** (0.3 mmol), 1 mL dry solvent, RGB LED stripe (~80 W) on green. [b]Yield determined by ^{1}H-NMR using 1,4-bis(trimethylsilyl)benzene as internal standard. [c]RGB LED stripe (~80 W) on blue. [d]Air was used instead of oxygen. [e]Isolated yield in brackets. [f]In the dark. [g]Argon instead of oxygen atmosphere.

Replacement of oxygen by air led to reduced conversion showing that a fast catalyst quenching is vital for fast reaction kinetics. Variation of the catalyst loading (entries 13 to 18) showed a faster reaction at lower catalyst loading, with 1 mol% as the optimum (entry 16). Most probably, at higher catalyst loading, light absorption is limited to a very small volume close to the surface of the vial and collision of excited catalyst with substrate molecules during the lifetime of the excited state is less likely. Further decreasing the catalyst loading resulted in a slightly decreased yield and conversion but a still satisfactory yield of 59% was achieved with only 0.1 mol% catalyst (entry 18), which is in good agreement with previous observations of organic dyes in part being highly efficient at even low catalyst loadings.[12a] In the absence of catalyst, light or oxygen the starting material remained untouched (entry 19 to 21). Various additives, light sources or variations of oxygen delivery were also taken into account in our studies but did not produce better results in terms of product yield or reaction time (see SI for further screenings).

With the improved reaction conditions, the scope of this reaction was evaluated (Scheme 2). A variety of functional groups were tolerated and moderate to high yields (**2b**, **2d-e**, **2j-l**, **2s**) could be achieved with electron donating and withdrawing groups such as Me, OMe, F, Cl, or CONHMe. Strongly electron withdrawing groups like CF_3 and NO_2 led to increased reaction times and lower yields (**2h**, **2i**). Even Br- and I-substituents were tolerated, although partial halogen transfer under formation of dihalogenated species was observed (**2f**, **2g**). In the case of the 3-carboxy substituted starting material, product **2t** was formed as the sole regioisomer. The moderate yield can be partly explained by the formation of **2t'** as a by-product, most probably caused by a Bayer-Villiger reaction of **2t** with H_2O_2 generated in the course of the reaction. At prolonged reaction times, over-oxidation to 4-pyridons and oxidative cleavage of the enaminone's C=C bond (vide supra) were frequently observed as side reactions of various substrates. The yields of 4-quinolones (**2o**, **2p**) were generally higher and in the range of 90%, which can be explained by increased product stability and fewer possibilities of side reactions such as over-oxidation. In addition, they provide better stabilization of the intermediates **9** and **10** (Scheme 3) which seem to be crucial for a rapid and clean reaction. On the other hand, *N*-alkyl substituents devoid of any stabilizing effect (**2u**) gave only unsatisfactory conversions, presumably due to the lower HOMO energy of the unconjugated nitrogen lone pair. The same was observed with *ortho*-substituents (**2w**, **2x**) which force the aromatic ring out of conjugation with the lone pair, leading to decreased orbital overlap according to DFT calculations (data not shown). *N*-1-naphthyl substituents are however tolerated in the reaction (**2p**, **2q**).

A plausible reaction mechanism is depicted in Scheme 3. After absorption of light, the catalyst **7** can react with substrate **1** to furnish the amine radical cation **9** by single-electron-transfer (SET). Upon reaction with molecular oxygen through a second SET step, the catalyst **7** is recycled leading to formation of a superoxide radical anion capable of abstracting a hydrogen from **9**.[17] By these means, the hydroperoxide anion and iminium ion



Scheme 2. Scope of cyclic enaminones by photocatalytic dehydrogenation. [a]Reaction conditions: **1** (0.3 mmol), 1 mL dry solvent, **7** (1 mol%), 1 atm O_2, RGB LED stripe (~80 W) on green, 25 °C. [b]Yield of recovered starting material. [c]No extraction performed due to high polarity of product. [d]As judged by ^{1}H-NMR.

10 is formed, the latter undergoes rapid deprotonation to the more stable enaminone **2** furnishing hydrogen peroxide as a by-product.

To demonstrate the synthetic value of this protocol, the reaction was performed on a gram scale (Scheme 4). For this purpose, a steady stream of oxygen was slowly bubbled through the solution to ensure sufficient availability of the oxidant. Besides an increase in reaction time, the dehydrogenation of **1a** proceeded smoothly to give the enaminone **2a** in 60% isolated yield.

With ample amounts of the cyclic enaminone **2** in hand, the [2+2] cycloaddition/ring-expansion sequence was to be optimized and the applicability of the photoredox-catalyzed dehydrogenation to the synthesis of azocinone derivatives had to be demonstrated (Table 2). The studies were begun using a modified protocol of the microwave assisted cycloaddition of

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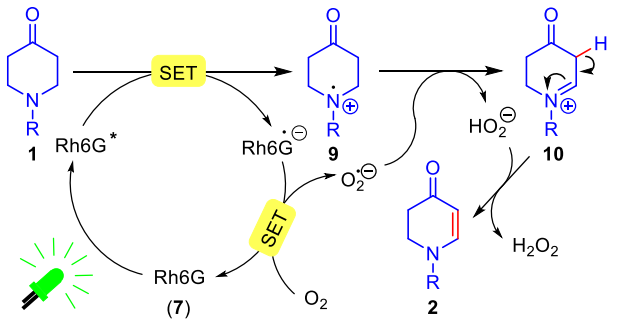
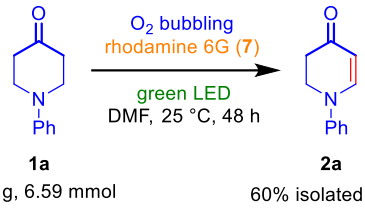
DMAD (**11a**) reported by the Stanovnik laboratory.[15b] With the aim to develop a one-pot reaction, rhodamine 6G (**7**) and DMF



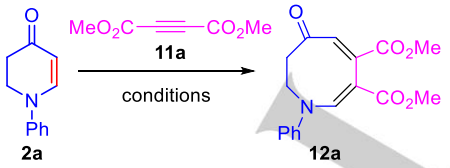
Scheme 3. Plausible reaction mechanism.



Scheme 4. Gram-scale synthesis of **2a**.

were added to all screening reactions to imitate the conditions after the dehydrogenation step. Indeed, the cycloaddition went smoothly to yield directly the eight-membered heterocycle **12a.** A short screening of co-solvents (entries 1 to 4) revealed acetonitrile to be the best choice of this group. Next, the reaction temperature was investigated. At higher temperature, the reaction was faster but a decrease in yield was observed (entry 5).

Table 2. Optimization studies for the photocatalytic dehydrogenation.[a]

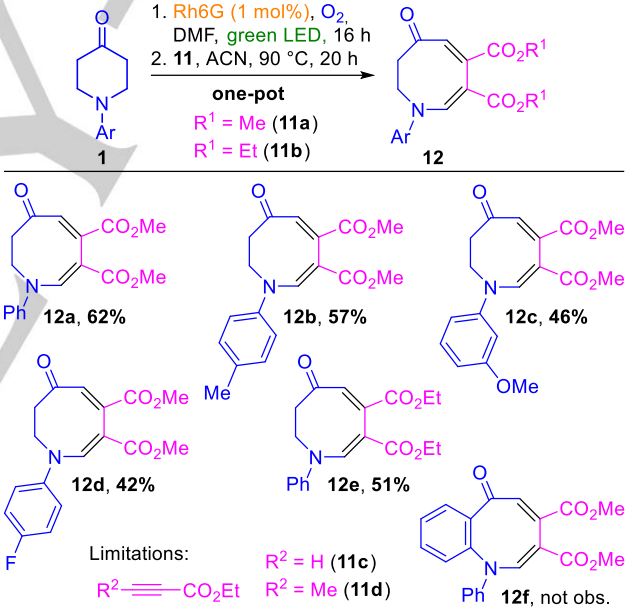


Entry	Co-solvent	Temp. (°C)	Time (h)	**2a** (%)[b]	**12a** (%)[b]
1	DMF	120	2	3	67
2	DCM	120	2	26	49
3	PhMe	120	2	25	53
4	ACN	120	2	4	74
5	ACN	150	1.5	3	68
6	ACN	105	6	12	79
7	ACN	90	17	7	88 (85) [c]
8	ACN	90	20	n.d.	(62) [c,d]

[a]Reaction conditions: **2a** (0.3 mmol), **7** (1 mol%), 1 mL DMF, 1 mL co-solvent, **11a** (3.0 eq.), sealed vessel, microwave irradiation. [b]Yield determined by ^{1}H-NMR using 1,4-bis(trimethylsilyl)benzene as internal standard, n.d. = not determined. [c]Isolated yields in brackets. Oil-bath instead of microwave. [d]One-pot reaction starting from **1a**.

Gradually decreasing the temperature led to longer reaction times but significantly increased yields. Finally, the best results were obtained when the reaction mixture was simply heated in an oil-bath overnight (entry 7). In the end, a telescoped one-pot reaction starting from **1a** was performed proving the possibility to access eight-membered *N*-heterocycles **12** directly from piperidones **1** (entry 8).

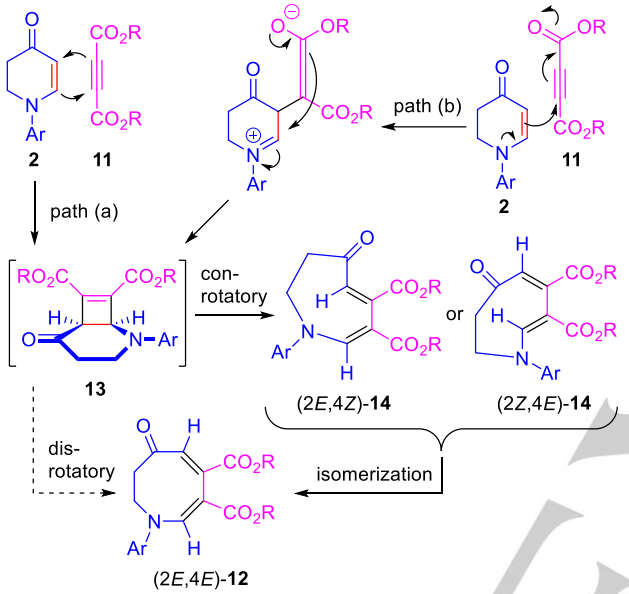
The scope of the one-pot synthesis of azocinones **12** from piperidones **1** and acetylene dicarboxylates **11** is displayed in Scheme 5. The reaction gave a variety of 2,3-dihydro-4-azocinones in synthetically useful yields (**12a-e**). It appeared tempting to investigate simple acetylenic esters **11c** and **11d** in the one-pot reaction of **1a**, but no conversion took place even at 120 °C and the enaminone **2a** was the only product isolated in both cases. Apparently, only very electron deficient acetylenes do react with **2**. Furthermore, we wondered whether benzo[*b*]azocinone **12f** could be obtained by reacting **1o** with **11a** in this sequence but again, only the 4-quinolone **2o** could be isolated. This observation might be explained by the high stability and hence low reactivity of the 4-quinolone **2o** so that no



Scheme 5. Scope of the one-pot synthesis of azocine-derivatives from piperidones. Reaction conditions: **1** (0.3 mmol), 1 mL dry DMF, **7** (1 mol%), 1 atm O_2, RGB LED stripe (~80 W) on green, 25 °C, then: 1 mL co-solvent, **11** (3.0 eq.), 90 °C, oil-bath.

cycloaddition takes place. A plausible mechanism of the cycloaddition/ring-expansion sequence is illustrated in Scheme 6. [2+2] cycloaddition of acetylene ester **11** and enaminone **2** furnish cyclobutene intermediate **13**. The cycloaddition can be either concerted (path a) or stepwise (path b).[15b] There had been some debate about the ring opening mechanism of *cis*-bicyclo[4.2.0]oct-7-ene-intermediates such as **13**.[18] The isolation of *cis*,*cis*-products in almost all cases has led to the assumption that ring opening may occur in a disrotatory fashion, which would violate

the Woodward-Hoffmann rules. However, some studies have shown that *trans*,*cis*-products can be obtained under carefully controlled and mild reaction conditions.[18c, 18d] Recent studies based on computational calculation revealed the conrotatory ring opening, followed by isomerization to be the most likely pathway.[18f] To determine the geometry of double bonds in **12a**, $^3J_{C\text{-}H}$ coupling constants between the methine protons and corresponding carbons were measured by CLIP-HSQMBC[19] and compared to literature values. Usually a *cis*-arrangement between C and H results in smaller values than in the case of a *trans*-arrangement (see Figure S2 in the SI).[20] From the measured



Scheme 6. Plausible mechanism of the cycloaddition/ring-expansion

values, the (2*E*,4*E*)-geometry was rationalized for **12a** which is consistent with the geometry of similar compounds.[15b, 18e] Although none of the intermediates **14** have been observed, we assume the mechanism to proceed by a conrotatory electrocyclic ring opening of **13.** The isomerisation to **12** in the cause of the reaction should be promoted by the push-pull character of intermediate **14**. The same geometry of **12** was obtained, when the reaction was performed either in a one-pot fashion starting from **1a** or from isolated **2a**, which shows that product geometry was not affected by any by-product from the previous dehydrogenation step, such as H_2O_2.

Conclusions

In summary, a mild and environmentally benign protocol for the synthesis of 2,3-dihydro-4-pyridones and 4-quinolones by means of visible-light mediated dehydrogenation using oxygen as a terminal oxidant and inexpensive rhodamine 6G as photocatalyst was developed. To the best of our knowledge, there is currently no cheaper and more sustainable way to effect this transformation. The reported methods tolerates a variety of functional groups and was successfully performed on a gram scale. In addition, it can be extended to access azocinones in a simple one-pot procedure. This versatile protocol could find application in the synthesis of natural products and drug precursors. Overcoming the necessity of *N*-aryl groups would make this method even more versatile and could eventually provide a general method to convert Mannich products into enaminones. Furthermore, better control of oxygen supply to increase efficiency and to avoid over-oxidation, potentially by means of flow chemistry, will remain as challenge for further investigations.

Experimental Section

General information: All chemicals were obtained from commercial suppliers and used without purification unless stated otherwise. Anhydrous DCM was distilled from calcium hydride under nitrogen. Anhydrous toluene and THF were distilled from sodium/benzophenone under nitrogen. Extra dry DMF, ACN, MeOH and DMSO were purchased from Acros Organics (AcroSeal®). The eluents for column chromatography ^{c}Hex and EtOAc were purchased in technical grade and distilled prior to use. Chloroform-*d* was stored over sodium sulfate and alumina (Brockmann activity I). Chromatographic purification was performed on silica gel (35–70 µm, Acros Organics). Automated flash chromatography was performed on an Isolera™ Flash Purification System (Biotage) with an integrated diode array detector using SNAP KP-Sil cartridges. TLC was carried out on silica plates (TLC Silica 60 F254 by Merck). NMR spectra were recorded on a Bruker Avance-III HD (^{1}H-NMR: 300 MHz, ^{13}C-NMR: 75.5 MHz), a Bruker Avance-II (^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100.6 MHz) or a Bruker Avance-III (^{1}H-NMR: 600 MHz, ^{13}C-NMR: 151.1 MHz) spectrometer. Chemical shifts are referenced to residual solvent signals ($CDCl_3$: 7.26 ppm and 77.16 ppm, DMSO-d_6: 2.50 ppm and 39.52 ppm for ^{1}H-NMR and ^{13}C-NMR respectively) and reported relative to TMS. IR spectra were recorded on a FTIR-spectrometer (Bruker Tensor 27) with a diamond ATR unit and are reported in terms of frequency of absorption $\tilde{\nu}$ [cm^{-1}]. ESI mass spectra were recorded on a 1200-series HPLC-system or a 1260-series Infinity II HPLC-system (Agilent-Technologies) with binary pump and integrated diode array detector coupled to a LC/MSD-Trap-XTC-mass spectrometer (Agilent-Technologies) or a LC/MSD Infinitylab LC/MSD (G6125B LC/MSD). HRMS spectra were recorded on a Micromass-Q-TOF-Ultima-3-mass spectrometer (Waters) with LockSpray-interface and a suitable external calibrant. Melting points were determined in open capillary tubes using a Krüss-Optronic KSP 1 N thermoelectric melting point meter. Reactions accelerated by microwave heating were performed in a Discover monomode apparatus from CEM in glass vials sealed with septa under constant temperature.

Compounds **1a-f**, **1h-i**, **1k-n**, **1q-s**,[21] **1i**,[22] **1o**,[23] **1p**,[23] and **1t**[24] were prepared by known procedures and their spectroscopic data are in accordance to those reported in the literature. Compounds **1u** and **1v** were obtained from commercial suppliers. Compound **1g**, **1j**, **1w** and **1x**[21] were prepared by known procedures but have not been characterized yet.

1-(4-iodophenyl)piperidin-4-one (1g): Yield: 64.9%, yellow solid; R_f = 0.39 (^{c}Hex/EtOAc = 3:1); mp: 98.1–100.2 °C; ^{1}H-NMR, COSY (400 MHz,

Chloroform-*d*) δ 7.57–7.52 (m, 2H, H3', H5'), 6.75–6.71 (m, 2H, H2', H6'), 3.58 (t, *J* = 6.1 Hz, 4H, H2, H6), 2.53 (t, *J* = 6.1 Hz, 4H, H3, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 207.75 (C4), 148.80 (C1'), 138.24 (C3', C5'), 117.89 (C2', C6'), 81.47 (C4'), 48.40 (C2, C6), 40.59 (C3, C5); IR: 2824, 1716, 1583, 1490, 1381, 1357, 1315, 1221, 1086, 989, 808; ESI-MS: 302.1 (100%) $[M+H]^+$; HRMS (ESI): m/z = 302.0034 ($[M+H]^+$, calc. 302.0036).

***N*-methyl-4-(4-oxopiperidin-1-yl)benzamide (1j):** Yield: 61.4%, yellow solid; R_f = 0.25 (100% EtOAc); mp: 134.6–137.6 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.74–7.69 (m, 2H, H3', H5'), 6.93–6.88 (m, 2H, H2', H6'), 6.30–6.17 (m, 1H, N*H*), 3.69 (t, *J* = 6.1 Hz, 4H, H2, H6), 2.97 (d, *J* = 4.8 Hz, 3H, CH_3), 2.54 (t, *J* = 6.1 Hz, 4H, H3, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) 207.65 (C4), 167.80 (*C*ONH), 151.03 (C1'), 128.73 (C3', C5'), 124.67 (C4'), 113.94 (C2', C6'), 47.28 (C2, C6), 40.46 (C3, C5), 26.86 (*C*H$_3$); IR: 3336, 2968, 2901, 1712, 1606, 1551, 1509, 1387, 1358, 1297, 1219, 768; ESI-MS: 233.2 (100%) $[M+H]^+$, 255.2 (38.5%) $[M+Na]^+$, 487.4 (20.9%) $[2M+Na]^+$; HRMS (ESI): m/z = 233.1282 ($[M+H]^+$, calc. 233.1285).

1-(*o*-tolyl)piperidin-4-one (1w): Yield: 70.4%, yellow solid; R_f = 0.21 (^{c}Hex/EtOAc = 20:1); mp: 66.9–68.7 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.25–7.21 (m, 1H, H3'), 7.21–7.16 (m, 1H, H5'), 7.06–7.01 (m, 2H, H4', H6'), 3.22 (t, *J* = 6.1 Hz, 4H, H2, H6), 2.61 (t, *J* = 6.1 Hz, 4H, H3, H5), 2.40 (s, 3H, CH_3); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 208.75 (C4), 150.81 (C1'), 132.72 (C2'), 131.25 (C3'), 126.74 (C5'), 123.89 (C4'), 119.48 (C6'), 52.11 (C2, C6), 42.28 (C3, C5), 17.94 (*C*H$_3$); ESI-MS: 190.2 (100%) $[M+H]^+$; HRMS (ESI): m/z = 190.1225 ($[M+H]^+$, calc. 190.1226).

1-(2-chlorophenyl)piperidin-4-one (1x): Yield: 31.7%, colorless solid; R_f = 0.50 (^{c}Hex/EtOAc = 3:1); mp: 83.1–83.5 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 7.9, 1.5 Hz, 1H, H3'), 7.23 (ddd, *J* = 8.0, 7.3, 1.5 Hz, 1H, H5'), 7.06 (dd, *J* = 8.0, 1.5 Hz, 1H, H6'), 7.04–6.99 (m, 1H, H4'), 3.34 (t, *J* = 6.1 Hz, 4H, H2, H6), 2.64 (t, *J* = 6.1 Hz, 4H, H3, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 208.52 (C4), 148.66 (C1'), 130.79 (C3'), 129.06 (C2'), 127.74 (C5'), 124.38 (C4'), 120.90 (C6'), 51.49 (C2, C6), 42.02 (C3, C5); IR: 2816, 1716, 1588, 1481, 1379, 1311, 1209, 1958, 1039, 756; ESI-MS: 210.1 (100%) $[M+H]^+$, 212.1 (43.0%) $[M+H]^+$; HRMS (ESI): m/z = 210.0680 ($[M+H]^+$, calc. 210.0680).

General procedure for the photoredox-catalyzed aerobic dehydrogenation: A 10 mL glass vial was charged with the 4-piperidone or 2,3-dihydro-4-quinolone **1** (0.300 mmol, 1.00 eq.), rhodamine 6G (**7**) (0.003 mmol, 1 mol%) and anhydrous DMF (1.00 mL). The vial was sealed with a rubber septum and the mixture was stirred until rhodamine 6G was completely dissolved. The reaction vessel was flushed with oxygen for 2 minutes and placed inside a flask, covered with LED stripes (see SI for irradiation setup). The mixture was stirred under irradiation with green LED stripes, until the starting material **1** was almost consumed completely (as judged by TLC or LC-MS analysis). Water was added and the mixture was extracted with Et_2O to remove most of the DMF. For **2j** and **2t** the extraction step was skipped due to the high polarity of these compounds. The organic phases were combined and the solvent was removed in vacuo. The crude product was purified by automated flash column chromatography (SiO_2, ^{c}Hex/EtOAc).

1-phenyl-2,3-dihydropyridin-4(1*H*)-one (2a): Yield: 36.4 mg, 0.210 mmol, 70%, orange solid; R_f = 0.24 (^{c}Hex/EtOAc = 2:3); mp: 89–90 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.8 Hz, 1H, H6), 7.43–7.33 (m, 2H, H3', H5'), 7.20–7.10 (m, 1H, H4'), 7.12–7.07 (m, 2H, H2', H6'), 5.22 (d, *J* = 7.8 Hz, 1H, H5), 4.00 (t, *J* = 8.1 Hz, 2H, H2), 2.65 (t, *J* = 8.1 Hz, 2H, H3); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 192.04 (C4), 149.71 (C6), 145.23 (C1'), 129.74 (C3', C5'), 124.47 (C4'), 118.29 (C2', C6'), 102.17 (C5), 47.66 (C2), 36.05 (C3); IR: 3058, 1645, 1572, 1494, 1315, 1219, 1178, 758, 694, 530; ESI-MS: 174.0 (100) $[M+H]^+$, 196.0 (20) $[M+Na]^+$. The analytical data are consistent with those reported in the literature.[2c]

1-(*p*-tolyl)-2,3-dihydropyridin-4(1*H*)-one (2b): Yield: 42.0 mg, 0.224 mmol, 75%, orange solid; R_f = 0.23 (^{c}Hex/EtOAc = 2:3); mp: 69.5–71.4 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.7 Hz, 1H, H2), 7.20–7.15 (m, 2H, H3', H5'), 7.01–6.96 (m, 2H, H2', H6'), 5.19 (d, *J* = 7.7 Hz, 1H, H3), 4.00–3.93 (m, 2H, H6), 2.66–2.60 (m, 2H, H5), 2.33 (s, 3H, CH_3); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 191.96 (C4), 150.01 (C2), 142.95 (C1'), 134.36 (C4'), 130.23 (C3', C5'), 118.46 (C2', C6'), 101.58 (C3), 47.88 (C6), 36.02 (C5), 20.81 (*C*H$_3$); IR: 1644, 1573, 1513, 1304, 1272, 1215, 1176, 1105, 1027, 800; ESI-MS: 188.1 (100%) $[M+H]^+$. The analytical data are consistent with those reported in the literature.[10o]

1-(4-methoxyphenyl)-2,3-dihydropyridin-4(1*H*)-one (2c): Yield: 22.0 mg, 0.108 mmol, 36.1%, yellow solid; R_f = 0.13 (^{c}Hex/EtOAc = 2:3); mp: 102.2–102.9 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) 7.34 (d, J = 7.7 Hz, 1H, H2), 7.06–7.02 (m, 2H, H2', H6'), 6.93–6.88 (m, 2H, H3', H5'), 5.17 (d, J = 7.7 Hz, 1H, H3), 3.95 (dd, J = 8.1, 7.2 Hz, 2H, H6), 3.81 (s, 3H, CH_3), 2.64 (dd, J = 8.1, 7.2 Hz, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 191.85 (C4), 156.97 (C4'), 150.57 (C2), 139.03 (C1'), 120.51 (C3', C5'), 114.90 (C2', C6'), 101.16 (C3), 55.73 (*C*H$_3$), 48.48 (C6), 36.05 (C5); IR: 1629, 1575, 1510, 1463, 1306, 1287, 1242, 1221, 1173, 1038, 806; ESI-MS: 204.1 (100%) $[M+H]^+$, 226.1 (30.7%) $[M+Na]^+$, 429.2 (35.7%) $[2M+Na]^+$. The analytical data are consistent with those reported in the literature.[10o]

1-(4-fluorophenyl)-2,3-dihydropyridin-4(1*H*)-one (2d): Yield: 32.4 mg, 0.169 mmol, 57%, orange solid; R_f = 0.12 (^{c}Hex/EtOAc = 2:3); mp: 110.2–113.4 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.35 (d, J = 7.8 Hz, 1H, H2), 7.09–7.04 (m, 4H, H2', H3', H5', H6'), 5.20 (d, J = 7.8 Hz, 1H, H3), 3.96 (dd, J = 8.1, 7.2 Hz, 2H, H6), 2.64 (dd, J = 8.1, 7.2 Hz, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 191.90 (C4), 159.72 (d, J = 244.9 Hz, C4'), 150.02 (C2), 141.69 (d, J = 2.9 Hz, C1'), 120.31 (d, J = 8.1 Hz, C2', C6'), 116.49 (d, J = 22.8 Hz, C3', C5'), 102.05 (C3), 48.20 (C6), 35.98 (C5); IR: 1632, 1577, 1508, 1316, 1306, 1276, 1214, 1181, 1164, 832, 818, 499; ESI-MS: 192.0 (100%) $[M+H]^+$, 214.0 (12.1%) $[M+Na]^+$. The analytical data are consistent with those reported in the literature.[10o]

1-(4-chlorophenyl)-2,3-dihydropyridin-4(1*H*)-one (2e): Yield: 39.4 mg, 63%, colorless solid; R_f = 0.27 (^{c}Hex/EtOAc = 1:4); mp: 98.7–99.8 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 7.8 Hz, 1H, H2), 7.35–7.30 (m, 2H, H3', H5'), 7.04–6.99 (m, 2H, H2', H6'), 5.22 (d, *J* = 7.8 Hz, 1H, H3), 3.99–3.92 (m, 2H, H6), 2.67–2.61 (m, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 191.91 (C4), 149.18 (C2), 143.81 (C1'), 129.75 (C3', C5'), 129.70 (C4'), 119.47 (C2', C6'), 102.74 (C3), 47.71 (C6),

35.97 (C5); IR: 3058, 2836, 1637, 1565, 1492, 1312, 1300, 1216, 1175, 1093, 798; ESI-MS: 208.0 (100%) $[M+H]^+$, 209.9 (32.8%) $[M+H]^+$; HRMS (APCI): m/z = 208.0525 ($[M+H]^+$, calc. 208.0524).

1-(4-bromophenyl)-2,3-dihydropyridin-4(1*H*)-one (2f): Yield: 24.8 mg, 33%, yellow solid; R_f = 0.17 (cHex/EtOAc = 2:3); mp: 122.6–124.5 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.50–7.46 (m, 2H, H3‘, H5‘), 7.38 (d, J = 7.8 Hz, 1H, H2), 7.00–6.94 (m, 2H, H2‘, H6‘), 5.24 (d, J = 7.8 Hz, 1H, H3), 3.97 (dd, J = 8.0, 7.1 Hz, 2H, H6), 2.66 (dd, J = 8.0, 7.1 Hz, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 191.93 (C4), 149.02 (C2), 144.30 (C1‘), 132.72 (C3‘, C5‘), 119.77 (C2‘, C6‘), 117.22 (C4‘), 102.93 (C3), 47.66 (C6), 36.02 (C5); IR: 1644, 1596, 1567, 1491, 1311, 1266, 1217, 1177, 821, 800; ESI-MS: 252.2 (99.5%), 254.0 (100%) $[M+H]^+$, 274.0 (9.2%), 276.0 (8.6%) $[M+Na]^+$; HRMS (APCI): m/z = 252.0019 ($[M+H]^+$, calc. 252.0019).

1-(4-iodophenyl)-2,3-dihydropyridin-4(1*H*)-one (2g): Yield: 20.0 mg, 0.0669 mmol, 22%, orange solid; R_f = 0.19 (cHex/EtOAc = 2:3); mp: 158.5–161.6 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.70–7.64 (m, 2H, H3‘, H5‘), 7.38 (d, J = 7.8 Hz, 1H, H2), 6.88–6.83 (m, 2H, H2‘, H6‘), 5.25 (d, J = 7.8 Hz, 1H, H3), 3.97 (dd, J = 8.0, 7.1 Hz, 2H, H6), 2.66 (dd, J = 8.0, 7.1 Hz, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 191.94 (C4), 148.84 (C2), 144.97 (C1‘), 138.67 (C3‘, C5‘), 120.05 (C2‘, C6‘), 103.10 (C3), 87.57 (C4‘), 47.55 (C6), 36.04 (C5); IR: 1649, 1594, 1572, 1488, 1312, 1299, 1264, 1247, 1218, 1177, 817; ESI-MS: 300.0 (100%) $[M+H]^+$, 322.0 (9.9%) $[M+Na]^+$; HRMS (APCI): m/z = 299.9878 ($[M+H]^+$, calc. 299.9880).

1-(4-(trifluoromethyl)phenyl)-2,3-dihydropyridin-4(1*H*)-one (2h): Yield: 20.7 mg, 0.0858 mmol, 29%, yellow solid; R_f = 0.19 (cHex/EtOAc = 2:3); mp: 119.2–121.8 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.66–7.62 (m, 2H, H3’, H5’), 7.47 (d, J = 7.8 Hz, 1H, H2), 7.19–7.16 (m, 2H, H2’, H6’), 5.32 (d, J = 7.8 Hz, 1H, H3), 4.07–4.01 (m, 2H, H6), 2.74–2.67 (m, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 192.04 (C4), 148.27 (C2), 147.72 (C1’), 127.10 (q, J = 3.7 Hz, C3’, C5’), 125.97 (q, J = 33.1 Hz, C4’)*, 124.07 (q, J = 271.5 Hz, CF_3)*, 117.54 (C2’, C6’), 104.08 (C3), 47.35 (C6), 36.08 (C5); *Outer quartet signals can hardly be seen due to their low intensity; IR: 1642, 1563, 1519, 1313, 1283, 1219, 1196, 1173, 1103, 1068; ESI-MS: 242.1 (100%) $[M+H]^+$, 264.0 (5.6%) $[M+Na]^+$; HRMS (APCI): m/z = 242.0793 ($[M+H]^+$, calc. 242.0787).

1-(4-nitrophenyl)-2,3-dihydropyridin-4(1*H*)-one (2i): Yield: 21.6 mg, 0.099 mmol, 33%, yellow solid; R_f = 0.26 (cHex/EtOAc = 1:4); mp: 125–135 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 8.30–8.22 (m, 2H, H3’, H5’), 7.52 (d, *J* = 8.0 Hz, 1H, H2), 7.20–7.13 (m, 2H, H2’, H6’), 5.40 (d, *J* = 8.0 Hz, 1H, H3), 4.11–4.06 (m, 2H, H6), 2.76–2.69 (m, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 191.96 (C4), 149.75 (C1’), 146.99 (C2), 143.19 (C4’), 125.86 (C3’, C5’), 116.84 (C2’, C6’), 105.71 (C3), 47.22 (C6), 36.04 (C5); IR: 1655, 1573, 1501, 1310, 1284, 1221, 1181, 1113, 854, 751; ESI-MS: 219.1 (100%) $[M+H]^+$. The analytical data are consistent with those reported in the literature.[25]

***N*-methyl-4-(4-oxo-3,4-dihydropyridin-1(2*H*)-yl)benzamide (2j):** Yield: 34.6 mg, 0.150 mmol, 50%, yellow solid; R_f = 0.19 (EtOAc/MeOH = 10:1); mp: 177.4–178.8 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.85–7.79 (m, 2H, H3‘, H5‘), 7.46 (d, J = 7.8 Hz, 1H, H2), 7.12–7.07 (m, 2H, H2‘, H6‘), 6.58 (q, J = 4.8 Hz, 1H, N*H*), 5.25 (d, J = 7.8 Hz, 1H, H3), 4.03–3.98 (m, 2H, H6), 2.97 (d, J = 4.8 Hz, 3H, CH_3), 2.68–2.62 (m, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 192.11 (C4), 167.15 (*C*O), 148.55 (C2), 147.22 (C1‘), 129.96 (C4‘), 128.73 (C3‘, C5‘), 117.26 (C2‘, C6‘), 103.44 (C3), 47.26 (C6), 35.99 (C5), 26.95 (CH_3); IR: 1636, 1563, 1504, 1409, 1304, 1277, 1218, 1178, 767, 728; ESI-MS: 231.2 (100%) $[M+H]^+$, 253.2 (47.5%) $[M+Na]^+$, 483.1 (19.9%) $[M+Na]^+$; HRMS (ESI): m/z = 231.1130 ($[M+H]^+$, calc. 231.1128).

1-(*m*-tolyl)-2,3-dihydropyridin-4(1*H*)-one (2k): Yield: 34.3 mg, 0.183 mmol, 62%, yellow oil; R_f = 0.25 (cHex/EtOAc = 2:3); ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.43 (d, J = 7.8 Hz, 1H, H2), 7.25 (td, J = 7.6, 0.7 Hz, 1H, H5’), 6.94–6.98 (m, 1H, H6’), 6.92–6.87 (m, 2H, H2’, H4’), 5.20 (d, J = 7.8 Hz, 1H, H3), 4.03–3.94 (m, 2H, H6), 2.68–2.59 (m, 2H, H5), 2.37 (s, 3H, CH_3); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 192.11 (C4), 149.86 (C2), 145.23 (C1’), 139.79 (C3’), 129.53 (C5’), 125.31 (C6’), 119.07 (C4’), 115.42 (C2’), 101.89 (C3), 47.70 (C6), 36.03 (C5), 21.65 (CH_3); IR: 1647, 1572, 1494, 1467, 1309, 1274, 1228, 1184, 778, 696; ESI-MS: 188.1 (100%) $[M+H]^+$, 210.0.1 (8.4%) $[M+Na]^+$, 397.1 (8.6%) $[2M+Na]^+$; HRMS (APCI): m/z = 188.1071 ($[M+H]^+$, calc. 188.1070).

1-(3-methoxyphenyl)-2,3-dihydropyridin-4(1*H*)-one (2l): Yield: 39.8 mg, 0.196 mmol, 65%, orange solid; R_f = 0.18 (cHex/EtOAc = 2:3); mp: 67.3–68.8 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.43 (d, J = 7.8 Hz, 1H, H2), 7.27 (t, J = 8.2 Hz, 1H, H5‘), 6.69–6.65 (m, 2H, H4‘, H6‘), 6.60 (t, J = 2.3 Hz, 1H, H2‘), 5.21 (d, J = 7.8 Hz, 1H, H3), 3.97 (dd, J = 8.1, 7.1 Hz, 2H, H6), 3.81 (s, 3H, CH_3), 2.64 (dd, J = 8.1, 7.1 Hz, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 192.20 (C4), 160.71 (C3‘), 149.66 (C2), 146.43 (C1‘), 130.53 (C5), 110.56, 109.37 (C4‘, C6‘), 104.76 (C2‘), 102.15 (C3), 55.52 (CH_3), 47.62 (C6), 35.99 (C5); IR: 1646, 1572, 1497, 1310, 1280, 1251, 1237, 1202, 1173, 1051; ESI-MS: 204.1 (100%) $[M+H]^+$, 226.1 (21.3%) $[M+Na]^+$, 429.3 (20.1%) $[2M+Na]^+$. The analytical data are consistent with those reported in the literature.[10o]

methyl 3-(4-oxo-3,4-dihydropyridin-1(2*H*)-yl)benzoate (2m): Yield: 26.3 mg, 0.114 mmol, 38%, yellow oil; R_f = 0.14 (cHex/EtOAc = 2:3); ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.79 (dt, *J* = 8.0, 1.2 Hz, 1H, H4’), 7.75 (dd, *J* = 2.6, 1.2 Hz, 1H, H2’), 7.46 (d, *J* = 7.8, 1H, H2), 7.45 (t, *J* = 8.0, 1H, H5’), 7.28 (ddd, *J* = 8.0, 2.6, 1.2 Hz, 1H, H6’), 5.26 (d, *J* = 7.8 Hz, 1H, H3), 4.03 (dd, *J* = 8.1, 7.1 Hz, 2H, H6), 3.92 (s, 3H, CH_3), 2.67 (dd, *J* = 8.1, 7.1 Hz, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 192.02 (C4), 166.38 (*C*OOMe), 149.08 (C2), 145.30 (C1’), 131.75 (C3’), 129.88 (C5’), 125.22 (C4’), 122.24 (C6’), 118.93 (C2’), 103.00 (C3), 52.54 (CH_3), 47.58 (C6), 36.02 (C5); IR: 1718, 1648, 1570, 1306, 1262, 1242, 1219, 1177, 1108, 755; ESI-MS: 232.1 (100%) $[M+H]^+$, 254.1 (30.2%) $[M+Na]^+$, 485.1 (18.6%) $[2M+Na]^+$; HRMS (ESI): m/z = 232.0971 ($[M+H]^+$, calc. 232.0968).

3-(4-oxo-3,4-dihydropyridin-1(2*H*)-yl)benzonitrile (2n): Yield: 23.7 mg, 0.120 mmol, 40%, yellow solid; R_f = 0.11 (cHex/EtOAc = 2:3); mp: 126.1–130.0 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.54–7.45 (m, 1H, H5‘), 7.42–7.38 (m, 2H, H2, H4‘), 7.36–7.30 (m, 2H, H2‘, H6‘), 5.30 (d, J = 7.9 Hz, 1H, H3), 4.05–3.97 (m, 2H, H6), 2.72–2.66 (m, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 191.82 (C4), 148.06 (C2), 145.70 (C1‘), 130.76 (C5‘), 127.34 (C4‘), 122.01 (C6‘), 120.91 (C2‘), 118.16 (*C*N), 113.89 (C3‘), 104.21 (C3), 47.38 (C6), 35.99 (C5); IR: 2230, 1647, 1570, 1490, 1464, 1311, 1277, 1225, 1178, 1112, 796; ESI-MS:

199.1 (100%) $[M+H]^+$, 221.0 (9.2%) $[M+Na]^+$; HRMS (APCI): m/z = 199.0871 ($[M+H]^+$, calc. 199.0866).

1-phenylquinolin-4(1*H*)-one (2o): Yield: 58.4 mg, 0.264 mmol, 88%, colorless solid; R_f = 0.07 (cHex/EtOAc = 2:3); mp: 124.5–126.2 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 8.43 (dd, *J* = 8.1, 1.6 Hz, 1H, H5), 7.61–7.51 (m, 4H, H2, H3', H4', H5'), 7.46 (ddd, *J* = 8.6, 7.0, 1.6 Hz, 1H, H7), 7.39–7.35 (m, 2H, H2', H6'), 7.32 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H, H6), 7.00–6.96 (m, 1H, H8), 6.33 (d, *J* = 7.8 Hz, 1H, H3); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 178.31 (C4), 142.80 (C2), 141.37, 141.35 (C8a, C1'), 131.90 (C7), 130.37 (C3', C5'), 129.57 (C4'), 127.60 (C2', C6'), 126.59 (C4a), 126.56 (C5), 123.92 (C6), 117.36 (C8), 110.22 (C3); IR: 1626, 1589, 1550, 1493, 1479, 1465, 1365, 1290, 1237, 769, 704; ESI-MS: 222.1 (100%) $[M+H]^+$, 465.2 (8.1%) $[2M+Na]^+$. The analytical data are consistent with those reported in the literature.[26]

1-(naphthalen-1-yl)quinolin-4(1*H*)-one (2p): Yield: 72.0 mg, 0.265 mmol, 89%, yellow solid; R_f = 0.15 (cHex/EtOAc = 2:3); mp: 174.2–178.3 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 8.54–8.44 (m, 1H, H5), 8.07 (dt, *J* = 8.4, 1.0 Hz, 1H, H4'), 8.00 (dt, *J* = 8.2, 1.0 Hz, 1H, H5'), 7.64 (dd, *J* = 8.4, 7.3 Hz, 1H, H3'), 7.60 (d, *J* = 7.7 Hz, 1H, H2), 7.59–7.54 (m, 2H, H2', H6'), 7.42 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H, H7'), 7.37–7.27 (m, 3H, H6, H7, H8'), 6.70–6.64 (m, 1H, H8), 6.41 (d, *J* = 7.7 Hz, 1H, H3); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 178.48 (C4), 143.35 (C2), 141.96 (C8a), 137.45 (C1'), 134.64 (C4a'), 132.10 (C7), 130.41 (C4'), 130.09 (C8a'), 128.71 (C5'), 128.14 (C7'), 127.37 (C6'), 126.54 (C4a), 126.51 (C5), 126.14 (C2'), 125.83 (C3'), 123.95 (C6), 122.16 (C8'), 117.63 (C8), 110.41 (C3); IR: 1624, 1606, 1590, 1551, 1478, 1395, 1365, 1289, 773, 729; ESI-MS: 272.1 (100%) $[M+H]^+$, 565.3 (11.1%) $[2M+Na]^+$; HRMS (ESI): m/z = 272.1073 ($[M+H]^+$, calc. 272.1070).

1-(naphthalen-1-yl)-2,3-dihydropyridin-4(1*H*)-one (2q): Yield: 27.5 mg, 0.123 mmol, 41%, brown solid; R_f = 0.20 (cHex/EtOAc = 2:3); mp: 90.0–98.9 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 8.05–8.01 (m, 1H, H8'), 7.94–7.91 (m, 1H, H5'), 7.82 (dt, *J* = 8.4, 1.1 Hz, 1H, H2'), 7.65–7.52 (m, 2H, H6', H7'), 7.48 (dd, *J* = 8.4, 7.3 Hz, 1H, H3'), 7.33 (d, *J* = 7.6 Hz, 1H, H2), 7.30 (dd, *J* = 7.3, 1.1 Hz, 1H, H4'), 5.27 (d, *J* = 7.6 Hz, 1H, H3), 3.99 (t, *J* = 7.6 Hz, 2H, H6), 2.92–2.63 (br m, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 192.10 (C4), 153.81 (C2), 142.73 (C1'), 134.83 (C4a'), 128.97 (C8a'), 128.85 (C5'), 127.88 (C2'), 127.27, 126.89 (C6', C7'), 125.73 (C3'), 122.45 (C8'), 121.77 (C4'), 101.26 (C3), 51.10 (C6), 36.57 (C5); IR: 1644, 1585, 1570, 1395, 1300, 1221, 1173, 1111, 799, 774; ESI-MS: 224.1 (100%) $[M+H]^+$, 246.1 (10.2%) $[M+Na]^+$, 469.1 (12.5%) $[2M+Na]^+$; HRMS (ESI): m/z = 224.1071 ($[M+H]^+$, calc. 224.1070).

1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2,3-dihydropyridin-4(1*H*)-one (2r): Yield: 24.6 mg, 0.106 mmol, 35%, orange needles; R_f = 0.24 (cHex/EtOAc = 1:4); mp: 163.3–170.9 °C; ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 7.7 Hz, 1H, H2), 6.85 (d, *J* = 8.7 Hz, 1H, H8'), 6.62 (d, *J* = 2.8 Hz, 1H, H5'), 6.59 (dd, *J* = 8.7, 2.8 Hz, 1H, H7'), 5.17 (d, *J* = 7.7 Hz, 1H, H3), 4.30–4.21 (m, 4H, H2', H3'), 3.95–3.88 (m, 2H, H6), 2.67–2.58 (m, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 191.96 (C4), 150.30 (C2), 144.12 (C4a'), 140.96 (C8a'), 139.63 (C6'), 118.03 (C8'), 112.09 (C7'), 108.31 (C5'), 101.39 (C3), 64.67, 64.40 (C2', C3'), 48.27 (C6), 36.04 (C5); IR: 1627, 1576, 1506, 1316, 1284, 1254, 1213, 1067, 894, 866; ESI-MS: 232.1 (100%) $[M+H]^+$, 254.2 (26%) $[M+Na]^+$, 485.2 (54%) $[2M+Na]^+$; HRMS (ESI): m/z = 232.0970 ($[M+H]^+$, calc. 232,0968).

1-(3,5-dimethylphenyl)-2,3-dihydropyridin-4(1*H*)-one (2s): Yield: 35.2 mg, 0.175 mmol, 58%, yellow oil; R_f = 0.18 (cHex/EtOAc = 2:3); ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.7 Hz, 1H, H2), 6.82–6.80 (m, 1H, H4'), 6.75–6.72 (m, 2H, H2', H6'), 5.21 (d, *J* = 7.7 Hz, 1H, H3), 3.99 (dd, *J* = 8.1, 7.1 Hz, 2H, H6), 2.64 (dd, *J* = 8.1, 7.1 Hz, 2H, H5), 2.34 (s, 6H, 2 x CH_3); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 192.11 (C4), 149.94 (C2), 145.23 (C1'), 139.52 (C3', C5'), 126.24 (C4'), 116.22 (C2', C6'), 101.64 (C3), 47.72 (C6), 36.01 (C5), 21.51 (2 x CH_3); IR: 1648, 1606, 1573, 1474, 1328, 1306, 1235, 1192, 1177, 840; ESI-MS: 202.1 (100%) $[M+H]^+$. The analytical data are consistent with those reported in the literature.[10o]

methyl 4-oxo-1-phenyl-1,4,5,6-tetrahydropyridine-3-carboxylate (2t): Yield: 20.9 mg, 0.0904 mmol, 30%, yellow oil; R_f = 0.14 (EtOAc = 100%); ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 8.51 (s, 1H, H2), 7.48–7.41 (m, 2H, H3', H5'), 7.31–7.27 (m, 1H, H4'), 7.25–7.21 (m, 2H, H2', H6'), 4.12–4.07 (m, 2H, H6), 3.80 (s, 3H, OCH_3), 2.76–2.70 (m, 2H, H5); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 186.93 (C4), 165.90 (COOMe), 156.60 (C1), 144.36 (C1'), 130.01 (C3', C5'), 126.73 (C4'), 119.81 (C2', C6'), 103.57 (C3), 51.70 (OCH_3), 48.27 (C6), 36.39 (C5); IR: 1720, 1666, 1571, 1494, 1386, 1323, 1257, 1202, 1147, 1071, 762; ESI-MS: 232.1 (100%) $[M+H]^+$, 254.1 (36.4%) $[M+Na]^+$, 485.2 (68.1%) $[2M+Na]^+$; HRMS (ESI): m/z = 232.0972 ($[M+H]^+$, calc. 232.0968).

methyl 7-oxo-4-phenyl-4,5,6,7-tetrahydro-1,4-oxazepine-2-carboxylate (2t'): Yield: 12.5 mg, 0.0506 mmol, 17%, yellow oil; R_f = 0.58 (cHex/EtOAc = 2:3); ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.62 (s, 1H, H3), 7.41–7.36 (m, 2H, H3', H5'), 7.20–7.15 (m, 1H, H4'), 7.14–7.10 (m, 2H, H2', H6'), 4.11–4.07 (m, 2H, H5), 3.81 (s, 3H, OCH_3), 3.12–3.09 (m, 2H, H6); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) 169.44 (C7), 164.38 (COOMe), 145.77 (C1'), 129.86 (C3', C5'), 128.39 (C3), 125.00 (C4'), 119.82 (C2', C6'), 119.69 (C2), 52.32 (OCH_3), 47.69 (C5), 35.41 (C6); IR: 1756, 1709, 1645, 1595, 1495, 1266, 1242, 1216, 1145, 756; ESI-MS: 248.1 (100%) $[M+H]^+$, 270.1 (28.0%) $[M+Na]^+$, 517.2 (49.5%) $[2M+Na]^+$; HRMS (ESI): m/z = 248.0920 ($[M+H]^+$, calc. 248.0917).

Gram scale procedure for the photoredox-catalyzed aerobic dehydrogenation: A 30 mL glass vial was charged with **1a** (1.15 g, 6.59 mmol, 1.00 eq.), rhodamine 6G (**7**) (0.0659 mmol, 1 mol%) and anhydrous DMF (22.0 mL). The mixture was stirred until rhodamine 6G was completely dissolved. A steady stream of oxygen was slowly bubbled through the solution (one bubble per second) using a disposable glass Pasteur pipet (see SI for irradiation setup). The mixture was stirred under irradiation with green LED stripes, until the starting material **1a** was almost consumed completely as judged by TLC and LC-MS analysis (careful monitoring the reaction progress is recommended to avoid over-oxidation). Water (50 mL) was added and the mixture was extracted with Et_2O (4 x 50 mL) to remove most of DMF. The organic phases were combined, dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography (SiO_2, cHex/EtOAc = 2:3) to yield **2a** (680.2 mg, 3.927 mmol, 60%).

General procedure for the one-pot synthesis of azocinones: The synthesis was performed according to the general procedure of the

dehydrogenation, with the following exception: After irradiation the reaction vessel was flushed with argon for 2 minutes, followed by addition of anhydrous ACN (1.00 mL) and the respective acetylene ester **11** (0.900 mmol, 3.00 eq.). The reaction mixture was heated at 90 °C in an oil bath for 20 h, followed by the usual work-up as described above.

dimethyl (2*E*,4*E*)-6-oxo-1-phenyl-1,6,7,8-tetrahydroazocine-3,4-dicarboxylate (12a): Yield: 58.2 mg, 0.185 mmol, 62%, orange resin; R_f = 0.50 (^{c}Hex/EtOAc = 2:3); ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.63 (s, 1H, H2), 7.39–7.32 (m, 2H, H3', H5'), 7.24–7.19 (m, 1H, H4'), 7.14–7.09 (m, 2H, H2', H6'), 6.63 (s, 1H, H5), 4.35 (s, 2H, H8), 3.79 (s, 3H, 4-CO_2CH_3), 3.62 (s, 3H, 3-CO_2CH_3), 2.56 (s, 2H, H7); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 205.67 (C6), 168.61 (3-*C*O), 168.27 (4-*C*O), 146.49 (C1'), 144.79 (C2), 134.12 (C4), 132.64 (C5), 129.83 (C3', C5'), 126.39 (C4'), 122.84 (C2', C6'), 97.23 (C3), 52.71 (4-CO_2CH_3), 51.78 (3-CO_2CH_3), 47.35 (C8), 38.72 (C7); IR: 1726, 1705, 1610, 1582, 1494, 1435, 1239, 1203, 1091, 1057; ESI-MS: 284.1 (39.5%) [M−OMe]$^+$, 316.1 (100%) [M+H]$^+$, 338.1 (44.8%) [M+Na]$^+$, 653.3 (39.3%) [2M+Na]$^+$; HRMS (ESI): m/z = 338.0994 ([M+Na]+, calc. 338.0999).

dimethyl (2*E*,4*E*)-6-oxo-1-(*p*-tolyl)-1,6,7,8-tetrahydroazocine-3,4-dicarboxylate (12b): Yield: 56.6 mg, 0.172 mmol, 57%, orang resin; R_f = 0.57 (^{c}Hex/EtOAc = 2:3); ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.61 (s, 1H, H2), 7.18–7.15 (m, 2H, H3', H5'), 7.03–6.98 (m, 2H, H2', H6'), 6.62 (s, 1H, H5), 3.92–3.67 (br m, 2H, H8), 3.81 (s, 3H, O*CH*$_3$), 3.63 (s, 3H, O*CH*$_3$), 2.55 (br m, 2H, H7), 2.33 (s, 3H, Ar*CH*$_3$); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 205.80 (C6), 168.72 (*C*O$_2$Me), 168.44 (*C*O$_2$Me), 145.18 (C2), 144.19 (C1'), 136.52 (C4'), 134.27 (C4), 132.43 (C5), 130.40 (C3', C5'), 123.09 (C2', C6'), 96.75 (C3), 52.75 (O*CH*$_3$), 51.79 (O*CH*$_3$), 47.58 (C8), 38.59 (C7), 20.95 (Ar*CH*$_3$); IR: 1726, 1704, 1581, 1511, 1434, 1305, 1238, 1202, 1090, 1057; ESI-MS: 298.1 (44.1%) [M−OMe]$^+$, 330.2 (100%) [M+H]$^+$, 352.2 (20.5%) [M+Na]$^+$, 681.3 (46.7%) [2M+Na]$^+$; HRMS (ESI): m/z = 352.1156 ([M+Na]$^+$, calc. 352.1155).

dimethyl (2*E*,4*E*)-1-(3-methoxyphenyl)-6-oxo-1,6,7,8-tetrahydroazocine-3,4-dicarboxylate (12c): Yield: 47.9 mg, 0.139 mmol, 46%, orange resin; R_f = 0.44 (^{c}Hex/EtOAc = 2:3); ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.65 (s, 1H, H2), 7.27 (t, *J* = 8.2 Hz, 1H, H5'), 6.76 (ddd, *J* = 8.2, 2.3, 0.8 Hz, 1H, H4'), 6.71 (ddd, *J* = 8.2, 2.3, 0.8 Hz, 1H, H6'), 6.67–6.60 (m, 2H, H5, H2'), 4.34 (br m, 2H, H8), 3.81 (s, 3H, CO_2CH_3), 3.80 (s, 3H, ArO*CH*$_3$), 3.64 (s, 3H, CO_2CH_3), 2.57 (br m, 2H, H7); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 205.62 (C6), 168.63 (*C*O$_2$Me), 168.32 (*C*O$_2$Me), 160.70 (C3'), 147.71 (C1'), 144.67 (C2), 134.25 (C4), 132.65 (C5), 130.61 (C5'), 114.93 (C6'), 111.53 (C4'), 109.07 (C2'), 97.37 (C3), 55.61 (ArO*CH*$_3$), 52.77 (CO_2CH_3), 51.85 (CO_2CH_3), 47.36 (C8), 38.86 (C7); IR: 1725, 1705, 1582, 1491, 1435, 1330, 1237, 1194, 1172, 1090, 1051, 777; ESI-MS: 314.1 (62.7%) [M−OMe]$^+$, 346.2 (100%) [M+H]$^+$, 368.1 (20.5%) [M+Na]$^+$, 713.3 (26.8%) [2M+Na]$^+$; HRMS (APPI): m/z = 346.1290 ([M+H]$^+$, calc. 346.1285).

dimethyl (2*E*,4*E*)-1-(4-fluorophenyl)-6-oxo-1,6,7,8-tetrahydroazocine-3,4-dicarboxylate (12d): Yield: 42.4 mg, 0.127 mmol, 42%, orange resin; R_f = 0.51 (^{c}Hex/EtOAc = 2:3); ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.53 (s, 1H, H3), 7.13–7.03 (m, 4H, H2', H3', H5', H6'), 6.65 (s, 1H, H5), 3.88–3.66 (br m, 2H, H8), 3.80 (s, 3H, C*H*$_3$), 3.63 (s, 3H, C*H*$_3$), 2.54 (br m, 2H, H7); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 205.58 (C6), 168.58 (*C*O$_2$Me), 168.22 (*C*O$_2$Me), 160.91 (d, *J* = 247.3 Hz, C4'), 144.97 (C2), 142.84 (d, *J* = 2.9 Hz, C1'), 133.97 (C4), 132.79 (C5), 125.34 (d, *J* = 8.2 Hz, C2', C6'), 116.73 (d, *J* = 22.8 Hz, C3', C5'), 97.33 (C3), 52.78 (*C*H$_3$), 51.87 (*C*H$_3$), 47.93 (C8), 38.49 (C7); IR: 1702, 1609, 1585, 1506, 1434, 1230, 1201, 1158, 1090, 1057, 730; ESI-MS: 302.1 (41.1%) [M−OMe]$^+$, 334.1 (100%) [M+H]$^+$, 356.1 (61.4%) [M+Na]$^+$, 689.3 (62.7%) [2M+Na]$^+$; HRMS (ESI): m/z = 334.1086 ([M+H]$^+$, calc. 334.1085).

diethyl (2*E*,4*E*)-6-oxo-1-phenyl-1,6,7,8-tetrahydroazocine-3,4-dicarboxylate (12e): Yield: 52.4 mg, 0.153 mmol, 51%, orange resin; R_f = 0.59 (^{c}Hex/EtOAc = 2:3); ^{1}H-NMR, COSY (400 MHz, Chloroform-*d*) δ 7.65 (s, 1H, H2), 7.40–7.34 (m, 2H, H3', H5'), 7.25–7.20 (m, 1H, H4'), 7.15–7.11 (m, 2H, H2', H6'), 6.63 (s, 1H, H5), 4.57–3.99 (m, 2H, H8), 4.27 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 4.10 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 2.58 (br m, 2H, H7), 1.32 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$), 1.20 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C-NMR, HSQC, HMBC (101 MHz, Chloroform-*d*) δ 205.89 (C6), 168.32 (*C*O$_2$Et), 167.92 (*C*O$_2$Et), 146.60 (C1'), 144.65 (C2), 134.72 (C4), 132.26 (C5), 129.87 (C3', C5'), 126.30 (C4'), 122.82 (C2', C6'), 97.79 (C3), 61.70 (O*C*H$_2$CH$_3$), 60.62 (O*C*H$_2$CH$_3$), 47.37 (C8), 38.90 (C7), 14.35 (OCH$_2$*C*H$_3$), 14.29 (OCH$_2$*C*H$_3$); IR: 1702, 1608, 1578, 1493, 1364, 1230, 1197, 1092, 1054, 1030, 757, 697; ESI-MS: 298.1 (45.7%) [M−OEt]$^+$, 344.2 (100%) [M+H]$^+$, 709.4 (44.8%) [2M+Na]$^+$; HRMS (ESI): m/z = 344.1496 ([M+H]$^+$, calc. 344.1492).

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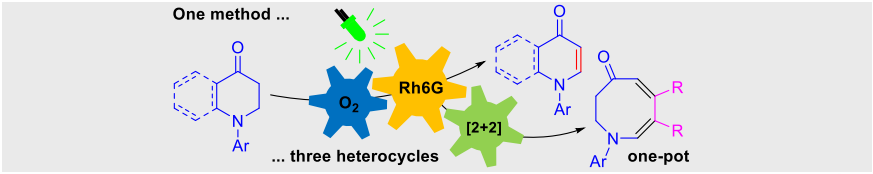

A protocol for the synthesis of three types of *N*-heterocycles was developed. Cyclic enaminones were prepared under eco-friendly conditions by photocatalytic dehydrogenation using rhodamine 6G as inexpensive photocatalyst and oxygen as the terminal oxidant. The method was extended to access azocinones *via* a [2+2] cycloaddition/ring-expansion sequence in a one-pot procedure.

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Photoredox catalysis*

*Adrian Sevenich, Paulina Sophie Mark, Torsten Behrendt, and Till Opatz**

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Synthesis of 2,3-Dihydro-4-Pyridones, 4-Quinolones and 2,3-Dihydro-4-Azocinones by Visible-Light Photocatalytic Aerobic Dehydrogenation