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Visible Light-Mediated Synthesis of (Spiro)anellated Furans

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Abstract: Visible light-mediated decarboxylation using *N*-acyloxyphthalimides as the source for carbon-centered radicals was applied for the synthesis of spirobutenolides. The utility of this approach is demonstrated with the formal synthesis of (*S*)-(+)-lycoperdic acid. Alternatively, 2,3-anellated furans can be obtained in a one-pot procedure *via* photocyclization following a regioselective semipinacol rearrangement.

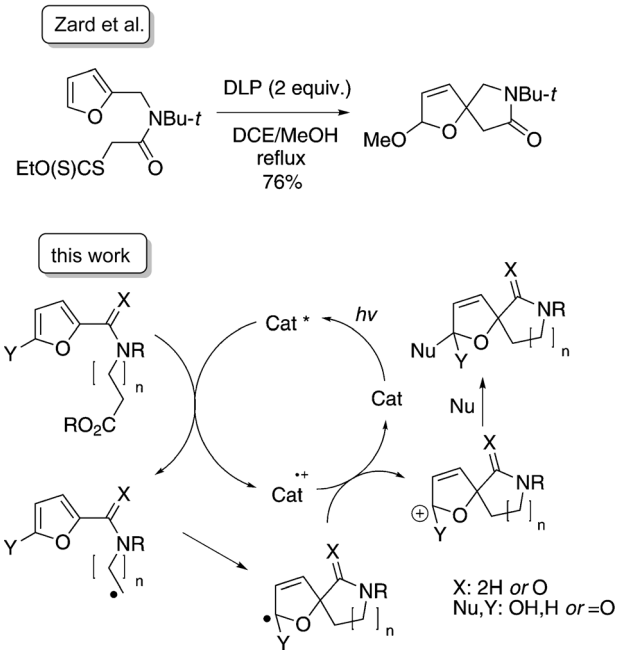
Keywords: butenolides; green chemistry; photoredox catalysis; semipinacol rearrangement; sensitization; spirocyclization

Introduction

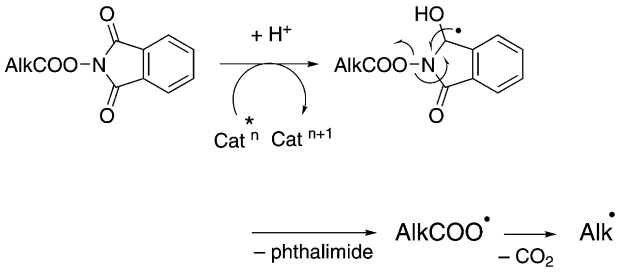
Visible light-mediated photoredox catalysis is an active research area of organic chemistry that meets the principles of green chemistry.[1] Several recent reviews[2] and publications[3] impressively document the potential for organic synthesis in this field. Another "green" approach highlights the exploitation of renewable resources, and especially simple furans or amino acids have been recognized as valuable starting materials.[4] A central theme in our research is focused on the development of methodology that allows the stereoselective dearomatization of furans or pyrroles to arrive at intermediates of relevance for fine chemicals or natural products and analogues.[5] In this study we demonstrate the application of visible light-mediated photoredox-catalyzed carbon-carbon bond forming reactions for the functionalization of furans, leading either to butenolides or anellated furans.

Zard et al. reported the oxidative dearomatization of furans *via* intramolecular radical spirocyclization (Scheme 1),[6] utilizing xanthates as precursors for α-keto radicals that are thermally generated in the presence of two equivalents of dilauroyl peroxide. We envisaged that a similar process should also be possible *via* a visible light-mediated photoredox-catalyzed pathway, and indeed, a great number of transformations have been recently developed by generating α-keto radicals from α-halo ketones or epoxy ketones in this way.[7] Nevertheless, we were looking for a more general precursor to generate a reactive radical intermediate, which led to the here reported development of visible light-initiated radical spirocyclizations onto furans starting from simple activated esters of carboxylic acids (Scheme 1).

Visible light-mediated redox transformations usually require substrates with low activation energies for electron transfer, being expressed by their redox po-



Scheme 1. Oxidative furan spirocyclizations.



Scheme 2. Redox photodecarboxylation of *N*-(acyloxy)-phthalimides.[9]

tentials, which results in the preferential formation of electron-deficient radicals.[8] However, the generation of alkyl radicals using this strategy was also reported: Okada et al.[9] and very recently Overman et al.[10] have demonstrated that *O*-acyl-*N*-hydroxyphthalimides could undergo cascade reductive decomposition accompanied with N–O bond cleavage followed by decarboxylation (Scheme 2) The resulting alkyl radicals could be trapped with various reagents (diselenide,[9a] Michael acceptors,[9b,10] CCl_4[9c] or thiols[9d]) completing the reaction.

Applying this strategy, we planned to combine furans (furoic acid, furfural, furfuryl amine etc.) with amino acids, overall merging green chemistry principles utilizing renewable resources and visible light-mediated photoredox catalysis.[11]

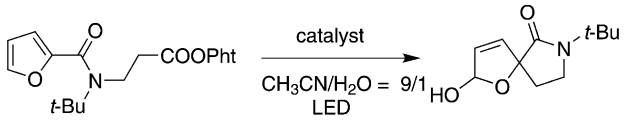
Results and Discussion

We started our investigation by screening catalysts (Table 1) on the readily available model compound **1a**.

Following the protocol developed by Okada et al, that calls for the combination of catalytic amounts of $Ru(bpy)_3Cl_2$[12] and 1.5 equivalents of 1-benzyl-l,4-dihydronicotinamide (BNAH) as sacrificial electron donor, thus utilizing the reductive quenching cycle Ru^+/Ru^{2+}, irradiation at 455 nm resulted in complete consumption of **1a**. However, rather than the desired decarboxylated and spirocyclized product **2a** only the formation of a complex mixture characterized by multiple spots on TLC was observed (entry 1). On the other hand in the absence of BNAH (thus attempting to utilize the oxidative quenching cycle $[Ru^{2+}]^*/Ru^{3+}$) no reaction at all was observed under otherwise indentical conditions (entry 2).

Since the excited catalyst is assumed to act as a reductant, we next turned our attention to $Cu(dap)_2Cl$[13a] [dap = 2,9-bis(*para*-anisyl)-1,10-phenanthroline] that is known to follow an oxidative quenching cycle in photoredox processes.[13] The desired product **2a** was indeed isolated in 40% yield (entry 3), but relatively high catalyst loading (5 mol%) and slow conversion led us seek further improvements. Among two types of iridium-based catalysts tested, $Ir(ppy)_2(dtbbpy)PF_6$ (dtbbpy = 4,4′-di-*tert*-butyl-2,2′-dipyridyl)[14] (entry 4) was found to be more effective, resulting at a loading of 1 mol% in the com-

Table 1. Catalyst screening.[a]

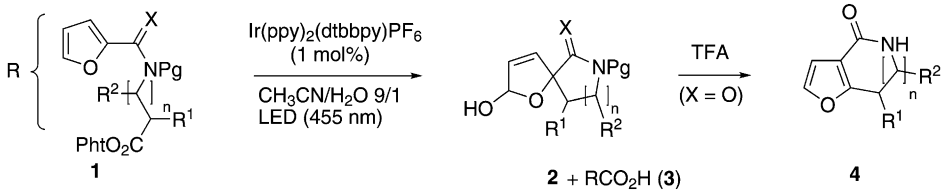


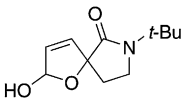
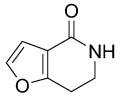
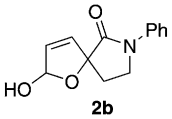
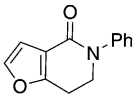
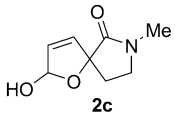
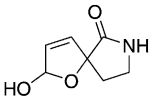
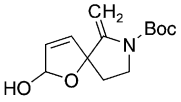
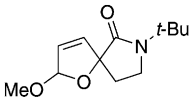
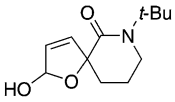
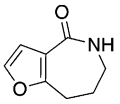
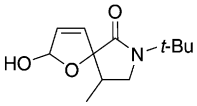
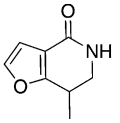
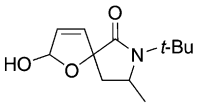
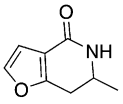
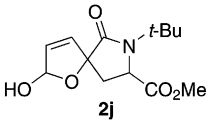
1a **2a**

Entry	Catalyst (mol%)	LED [nm]	Time [h]	Conversion (yield)[a] [%]
1[b]	$Ru(bpy)_3Cl_2$ (2.5)	455	24	100 (0)
2	$Ru(bpy)_3Cl_2$ (2.5)	455	24	0 (0)
3	$Cu(dap)_2Cl$ (5)	420	24	80 (40)
4	$Ir(ppy)_2(dtbbpy)PF_6$ (1)	455	8	100 (61)
5	$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1)	420	15	70 (–)
6[c]	perylene (15)	420	45	100 (43)
7	no catalyst	455	8	0 (0)
8[d]	$Ir(ppy)_2(dtbbpy)PF_6$ (1)	–	8	0 (0)
9[e]	$Ir(ppy)_2(dtbbpy)PF_6$ (1)	455	8	0 (0)
10[f]	$Ir(ppy)_2(dtbbpy)PF_6$ (1)	455	18	20 (0)

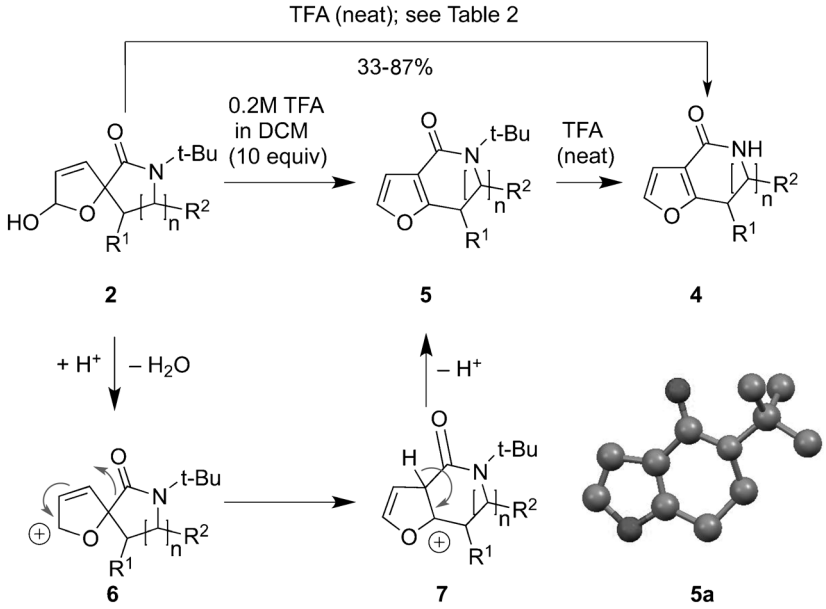
[a] Conversion was estimated by NMR; isolated yields after chromatography; Pht = phthalimid-2-yl).
[b] In the presence of 1.5 equiv. BNAH.
[c] In THF/water = 8/1.
[d] Without irradiation.
[e] In anhydrous acetonitrile.
[f] Without degassing.

Table 2. Scope of the reaction.[a]



Entry	**2**	Time [h][b]	Yield of **2** [%][c]	**4**	Overall yield of **4** without isolation of **2** [%][c]
1	 **2a**	8	61	 **4a**	84 (70)[d]
2	 **2b**	20	35	 **4b**	31
3	 **2c**	43	21	N/A	–
4	 **2d**	24	0[e]	N/A	–
5	 **2e**	18	50	N/A	–
6	 **2f**	18	55[f] (*dr* 1/1)	N/A	–
7	 **2g**	18	55	 **4g**	43
8	 **2h**	18	42[f] (*dr* 1/1)	 **4h**	87
9	 **2i**	18	38[f] (*dr* 3/2)	 **4i**	53
10	 **2j**	18	35[f] (*dr* 1/1)	N/A	–

[a] *Reaction conditions:* **2** (0.1–2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol%) in $CH_3CN/H_2O = 9/1$ (0.05 M concentration) and irradiation with 1W LED (455 nm); Pht = phthalimid-2-yl. [b] Full conversion time, monitored by TLC. [c] Isolated yield after chromatography. [d] 10 mmol scale, 0.5 mol% catalyst. [e] 60% conversion, **2d** was not detected; acid **3** was the main product. [f] Combined yield for two diastereomers; ratio was estimated by NMR of crude.



Scheme 3. Vinylogous semipinacol rearrangement of **2**.

plete conversion of **1a** within 8 h, giving rise to **2a** in 61% yield.

In contrast, using $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ [$dF(CF_3)ppy$ = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine][15] a much slower conversion was observed (entry 5). Perylene (entry 6), which shows a strong absorption at 435 nm (together with only 3 nm of Stokes shift) and has a promising redox potential in ground state[16] required a loading of 15 mol% and prolonged reaction time (45 h) in order to achieve a comparable yield (43%) of **2a**. No conversion of **1a** in the absence of catalyst, light or water was observed (entries 7–9), moreover, the presence of oxygen leads to slow consumption of starting material, but no product formation was observed (entry 10).

Having identified $Ir(ppy)_2(dtbbpy)PF_6$ as the best catalyst for the transformation, we examined the scope of the reaction (Table 2). The substitution pattern on nitrogen in **1** played a crucial role, revealing that sterically bulky groups favour the desired spirocyclization to **2**, being in agreement with the Thorpe–Ingold[17] effect (entries 1–4). Substituents R^1 and R^2 are tolerated well in the β-amino acid part of **1**, opening the possibility for stereocontrol in the spirocyclization process (entries 8–10). However, the two diastereomers of **2h** and **2j** were formed with little preference for one over the other, pointing towards an early transitions state in the cyclization step. Besides the spiroanellation of pyrrolidinones, the formation of pyrrolidines is also possible (entry 5). Water was generally used as the terminal nucleophile, however, the use of methanol leading to acetal **2f** is also possible (entry 6). Moreover, the 6-spiroanellated **2g** could be obtained from one-carbon extended homologue **1g** by an analogous 6-*exo*-trig cyclization (entry 7).

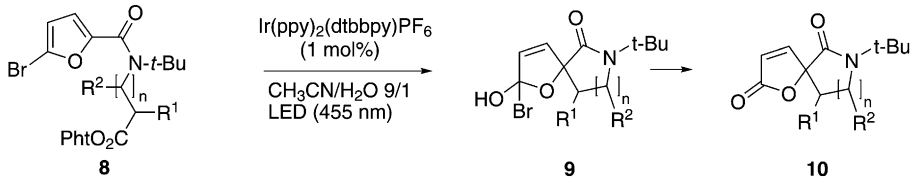
The competing reaction pathway is the formation of the carboxylic acid **3**, which could be considered to arise from simple hydrolysis. However, since **1** is stable under the reaction conditions in the dark and based on the presence of *N*-phthalimide rather than *N*-hydroxyphthalimide in the reaction mixture after irradiation, we assume that **3** is a product of a photoprocess as well (see mechanistic discussion below, Scheme 5).

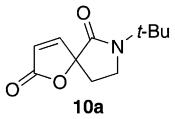
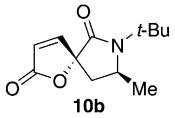
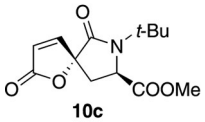
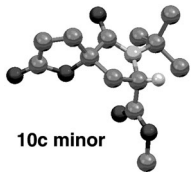
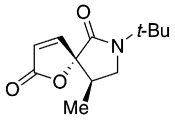
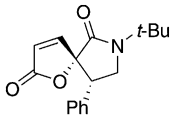
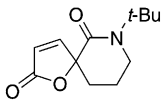
Besides the competing formation of **3** the moderate yields of the spiroanellated **2** were also due to the low stability of the latter. Turning this to an advantage, **2** can be readily transformed by a vinylogous semipinacol[18] rearrangement to **4**, in which selectively the acyl group undergoes a 1,2-shift with concurrent reformation of the furan moiety (Scheme 3).[19] The X-ray structure analysis of **5a** unambiguously proved the course of this reaction (CCDC 944711, these data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif).

Starting from **1** the overall process, that is, photocyclization and rearrangement can be carried out in a one-pot process, which gives rise to **4** in improved yields with respect to **2** (Table 2). The efficiency of this protocol was demonstrated on a 10-mmol scale reaction giving a 70% isolated yield of **4a** after 48 h of irradiation and only 0.5 mol% loading of the iridium catalyst (entry 1).

Alternatively, the spirolactols **2** could be easily oxidized (not shown) following a literature precedent[20] into butenolides **10**, a motif present in various natural

Table 3. Butenolide synthesis.[a]

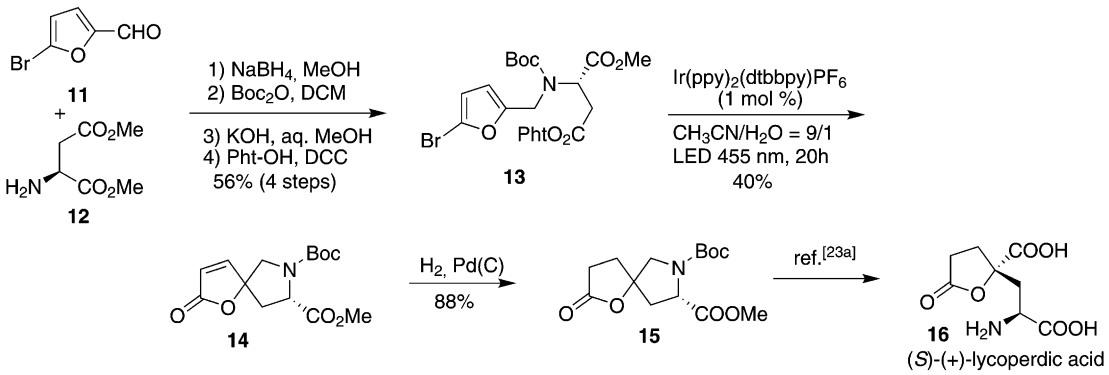


Entry	Product[b]	Yield [%][c]	*dr*[d]
1	 **10a**	52	N/A
2	 **10b**	61[e]	2/1
3	 **10c**  **10c minor**	51[e]	3/2
4	 **10d**	50[f]	2/1
5	 **10e**	19[e]	2/1
6	 **10f**	48	N/A

[a] *Reaction conditions:* **8** (0.1–1 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (1 mol%) in $CH_3CN/H_2O = 9/1$ (0.05 M concentration) and 18 h irradiation with 1W LED (455 nm); Pht = phthalimid-2-yl.
[b] Structure of the major diastereomer is shown.
[c] Isolated yield after chromatography.
[d] Ratio was estimated by NMR of crude.
[e] Combined yield for two separable diastereomers.
[f] Combined yield for two inseparable diastereomers.

products.[21] However, using the strategy presented here, a more direct approach to **10** could be developed (Table 3). Starting from 5-bromofuroic acid derivatives **8** instead of **2**, the analogous photocyclization led to the bromolactols **9**, which collapse upon elimination of HBr directly to the desired butenolides **10** with overall improved yields compared to the formation of lactols **2**. Again, if the β-amino acid chain in **8** possesses substituents, **10** is formed as a separable (with the exception of **10d**) mixture of two diastereomers, which could be assigned by NOESY NMR measurements and by an X-ray structure of the minor diastereomer formed in **10c** (entry 3) (CCDC 944712, these data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

An application of this strategy is demonstrated with the formal synthesis of (*S*)-(+)-lycoperdic acid (**16**, Scheme 4).[22,23] The key intermediate **13**, readily available in four steps from commercially available 5-bromofurfural (**11**) and (*S*)-aspartic acid dimethyl ester (**12**) was photocyclized under the established conditions to give rise to butenolide **14** in 40% yield. Upon hydrogenation a 2:1 mixture of the diasteromeric bu-



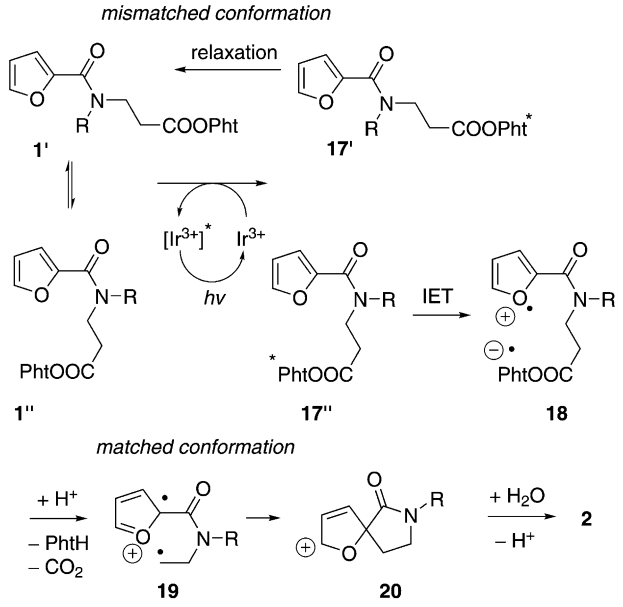
Scheme 4. Formal synthesis of (*S*)-(+)-lycoperdic acid.

tyrolactones **15** was obtained, which can be transformed to (*S*)-(+)-lycoperdic acid by the route described by Yoshifuji et al.[23a]

The process described here requires both irradiation and a photocatalyst, and $Ir(ppy)_2(dtbbpy)PF_6$ was identified to be most efficient. Analyzing the reducing power of the latter after excitation, ($*Ir^{3+} \rightarrow Ir^{4+} = -0.96$ V *vs.* SCE)[15] with that of **1a** (−1.25 V *vs.* SCE, see the Supporting Information)[24] reveals that an oxidative quenching cycle for the title transformation is thermodynamically difficult.[8] Likewise, the potential of $*Ru(bpy)_3^{2+}$ (−0.87 V *vs.* SCE)[8] is out of the range to induce an PET to **1a** (Table 1, entry 2). Moreover, due to the absence of a suitable electron donor that could act as a reductant for these catalysts, a reductive quenching cycle can also be ruled out. Indeed, Sammis et al.[25] recently showed that *N*-alkoxyphthalimides can be cleaved by visible light irradiation of $Ru(bpy)_3(PF_6)_2$ in the presence of a sacrificial electron donor, thus utilizing the reductive quenching cycle [Ru^{+}/Ru^{2+} (−1.35 V (*vs.* SCE)[8]] (*cf.* Table 1, entry 1).[26]

Nevertheless, spectroscopic measurements on $Ir(ppy)_2(dtbbpy)PF_6$ revealed that the fluorescence of the catalyst could be quenched by **1** suggesting an electron or energy transfer from the excited triplet state of the catalyst. Since the redox pathway is considered to be difficult, we propose that $Ir(ppy)_2(dtbbpy)PF_6$ acts as a sensitizer,[27] transferring energy from its excited state to the phthalimide moiety in **1** generating its triplet state **17** with a significantly higher redox potential.[28] Possessing a suitable conformation (**17″**), intramolecular electron transfer (IET) from a furan moiety could occur[29] to give rise to the intermediate **18**, which after protonation undergoes N−O bond homolytic cleavage, followed by decarboxylation and radical recombination[30] leading to the spirocation **20** (Scheme 5). The sensitization mechanism is supported *via* direct excitation of the phthalimide moiety by UV irradiation of **1a**, giving rise to **2a** in 45% yield (see the Supporting Information). Furthermore, the observed influence of the N-substituent in **1** on the yield and reaction time (Table 2, entries 1–4) points towards the necessity of a suitable conformation being populated to a significant extent for the IET to take place. Noteworthy, a similar sensitization of phthalimide from the triplet state of acetone was proposed by Griesbeck for the explanation of a photo-Kolbe type transformation.[28,30]

However, as estimated from the emission spectrum the triplet energy of **1** is considerably higher (approx. 3.1 eV)[28] than that of $Ir(ppy)_2(dtbbpy)PF_6$ (2.17 eV)[15,14] making a fluorescence resonance energy transfer (FRET or sensitization) also difficult. Also, the formation of by-product acid **3**, which in absence of *N*-hydroxyphthalimide cannot arise from simple hydrolysis but must involve a photoreduction process, is not clear. Finally, it must be pointed out that $Cu(dap)_2Cl$ (*cf.* Table 1) would have a suitable



Scheme 5. Mechanistic discussion.

redox potential [$*Cu(dap)^+/Cu(dap)^{2+} = -1.43$ V *vs.* SCE][13a] to allow a PET process to **1**, and while indeed the conversion of **1a** to **2a** was achieved with this catalyst (Table 1, entry 3), its efficiency was much lower than that of $Ir(ppy)_2(dtbbpy)PF_6$.

Conclusions

In conclusion, we have developed visible light-mediated transformations of activated carboxylic acids catalyzed by $Ir(ppy)_2(dtbbpy)PF_6$, presumably acting as a sensitizer. The methodology was applied to the synthesis of spirobutenolides, demonstrating a formal total synthesis of (*S*)-(+)-lycoperdic acid. Additionally, an acid-catalyzed vinylogous semipinacol rearrangement of the initially formed spirobutenolides was discovered, allowing the anellation of cyclic lactams onto a furan moiety.

Experimental Section

Typical Procedure for the Photodecarboxylative Spirocyclization of 1 to 2; Synthesis of 7-*tert*-Butyl-2-hydroxy-1-oxa-7-azaspiro[4.4]non-3-en-6-one (2a)

A 50-mL flask equipped with a magnetic stir bar and septum was charged with **1a** (484 mg, 1.26 mmol) and [Ir(dtb-bpy)(ppy)$_2$]PF_6·H_2O (12.0 mg, 0.013 mmol) in 25 mL of acetonitrile/water 9/1 mixture (0.05 M concentration). The solution was degassed using three freeze-pump-thaw cycles and stirred at room temperature at a distance of approximately 2 cm from a blue light emitting diode (LED) (λ_{max} = 455 nm) for 8 h (TLC monitoring). After the starting material had been consumed the solvent was removed under reduced pressure. The residue was purified on silica to afford **2a**; yield: 162 mg (61%); R_f = 0.20 (DCM/Et_2O = 5/1). ^{1}H NMR (300 MHz, $CDCl_3$, anomeric mixture ~9/1): δ = 6.26 (d, J = 6.7 Hz, 0.1 H) and 5.88 (d, J = 11.5 Hz, 0.9 H), 6.13 (dt, J = 5.8, 0.5 Hz, 0.9 H) and 6.02 (dd, J = 5.8, 1.0 Hz, 0.1 H), 5.97 (dd, J = 5.8, 1.0 Hz, 0.1 H) and 5.93 (dd, J = 5.8, 0.5 Hz, 0.9 H), 4.36 (d, J = 11.5 Hz, 0.9 H), 4.19 (br.s, 0.1 H), 3.57 (ddd, J = 10.0, 7.6, 4.5 Hz, 1 H) and 3.55–3.48 (m, 0.1 H), 3.42 (dt, J = 10.0, 7.6 Hz, 1 H) and 3.41–3.32 (m, 0.1 H), 2.32–2.17 (m, 2 H), 1.400 (s, 8 H) and 1.395 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major anomer): δ = 173.2, 132.2, 131.0, 102.7, 92.4, 55.1, 42.2, 28.3, 27.5; HR-MS: (ESI-MS): m/z = 212.1281, calculated for $C_{11}H_{17}NO_3$ [M+H]: 212.1281. In addition, 176 mg (95%) of phthalimide (R_f = 0.48, DCM/Et_2O = 10/1) were isolated.

Typical Procedure for the One-Pot Transformation of 1 to 4; Synthesis of 7-Methyl-6,7-dihydrofuro[3,2-*c*]pyridin-4(5*H*)-one (4h)

A 50-mL flask equipped with a magnetic stir bar and septum was charged with **1h** (800 mg, 2.01 mmol) and [Ir(dtb-bpy)(ppy)$_2$]PF_6·H_2O (19.4 mg, 0.021 mmol) in 20 mL of acetonitrile/water 9/1 mixture (0.1 M concentration). The solution was degassed using three freeze-pump-thaw cycles and stirred at room temperature at a distance of approximately 2 cm from a blue light emitting diode (LED) (λ_{max} = 455 nm) for 18 h (TLC monitoring). After the starting material had been consumed the solvent was removed under reduced pressure. The residue was dissolved in TFA (1 mL/0.1 mmol). The resulting solution was stirred at room temperature overnight, concentrated, dissolved in DCM, washed with $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated again. The product was purified on silica to afford **4h**; yield: 263 mg (87%); R_f = 0.10 (DCM/MeOH = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, J = 2.0 Hz, 1 H), 6.71 (d, J = 2.0 Hz, 1 H), 6.04 (br.s, 1 H), 3.62 (dd, J = 12.0, 5.8 Hz, 1 H), 3.28 (dd, J = 12.0, 9.0 Hz, 1 H), 3.25–3.16 (m, 1 H), 1.32 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 163.3, 142.6, 114.1, 107.8, 47.7, 28.9, 15.0; HR-MS (ESI-MS): m/z = 152.0709, calculated for $C_8H_9NO_2$ [M+H]: 152.0706.

Typical Procedure for the Spirocyclization of 8 to 10; Synthesis of 7-*tert*-Butyl-1-oxa-7-azaspiro[4.5]dec-3-ene-2,6-dione (10f)

A 50-mL flask equipped with a magnetic stir bar and septum was charged with **8f** (477 mg, 1.00 mmol) and [Ir(dtb-bpy)(ppy)$_2$]PF_6·H_2O (9.3 mg, 0.01 mmol) in 20 mL of acetonitrile/water 9/1 mixture (0.05 M concentration). The solution was degassed using three freeze-pump-thaw cycles and stirred at room temperature at a distance of approximately 2 cm from a blue light emitting diode (LED) (λ_{max} = 455 nm) for 18 h (TLC monitoring). After the starting material had been consumed the solvent was removed under reduced pressure. The residue was purified on silica to afford **10f**; yield: 107 mg (48%); R_f = 0.21 (EtOAc/hexanes = 1/1). ^{1}H NMR (300 MHz, $CDCl_3$, anomeric mixture ~9/1): δ = 7.34 (d, J = 5.7 Hz, 1 H), 6.17 (d, J = 5.7 Hz, 1 H), 3.56–3.47 (m, 1 H), 3.46–3.36 (m, 1 H), 2.18–2.02 (m, 3 H), 2.01–1.87 (m, 1 H), 1.42 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.4, 164.4, 155.9, 122.0, 87.8, 58.6, 44.4, 31.3, 27.9, 20.5; HR-MS (ESI-MS): m/z = 224.1285, calculated for $C_{12}H_{17}NO_3$ [M+H]: 224.1281.

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