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A Photoinduced Cobalt-Catalyzed Synthesis of Pyrroles through *in Situ*-Generated Acylazirines

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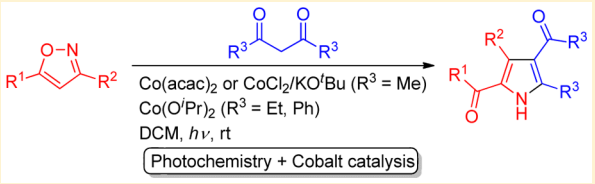
Supporting Information

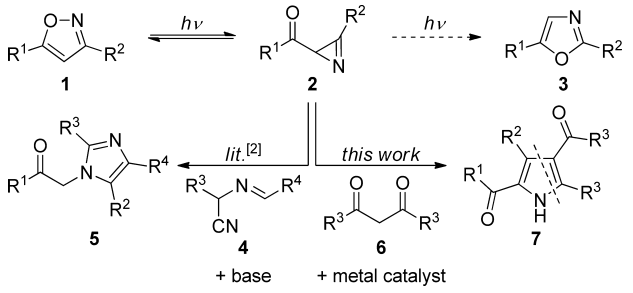
ABSTRACT: Tetrasubstituted pyrroles can be synthesized in a one-pot procedure from isoxazoles. The process includes the photoinduced *in situ* formation of acylazirines combined with a subsequent cobalt(II)-catalyzed ring expansion with 1,3-diketones.



INTRODUCTION

An attractive strategy for the construction of heterocycles is the utilization of ring strain present in small-ring systems.[1] Ideally, these high-energy compounds are generated as intermediates *in situ* from stable precursors and are directly transformed into the desired heterocyclic products under the conditions of their formation. This methodology would obviate the use of kinetically stable intermediates if the subsequent step is faster than a competing uncatalyzed transformation of the intermediate and could even be utilized to synthesize compounds with an energy content higher than that of the original starting material. Thus, the formation of low-energy coproducts such as borates, trialkyltin halides, or ureas resulting from classical C−C− and C−heteroatom bond formations could be circumvented. Recently, we developed a one-pot synthesis of tetrasubstituted imidazoles **5** from acylazirines **2** generated *in situ* by a photochemical ring transformation of isoxazoles **1** (Scheme 1).[2]

Scheme 1. Isomerization of Isoxazoles to Azirines/Oxazoles, Previously Reported Base-Mediated Imidazole Synthesis, and Envisioned Metal-Catalyzed Pyrrole Synthesis



The photochemical isomerization of isoxazoles **1** to corresponding acylazirines **2** is well-known,[3] but the maximally achievable yield of azirine **2** itself is limited because of the competing irreversible formation of oxazoles **3** as byproducts unless an efficient secondary reaction on intermediates **2** is established. While the synthesis of imidazoles **5** from acylazirines **2** was achieved in high yield by reaction with α-(alkylideneamino)-nitriles **4** formed from aldehydes and α-aminonitriles in a one-pot procedure, we also intended to combine the photochemical activation step with transition metal catalysis. Such a dual activation appears to be very attractive in terms of the accessible products as well as in terms of resource efficiency by minimizing the amount of undesired coproducts. A prerequisite for dual photo- and metal catalysis is the compatibility of the employed catalyst with the photoactivation of the substrate. The stability of common transition metal catalysts against UV light is not an issue in standard catalysis, but it must be taken into account in the described setting, as most catalytically active transition metal complexes do not provide sufficient transparency in the spectral range required for substrate photoactivation. As a case study for the feasibility of the dual activation approach, we sought a route by which to synthesize 2,4-diacyl-substituted pyrroles **7** from intermediates **2** by condensation with 1,3-diketones **6**.

Pyrroles make up an important class of heterocyclic compounds and are present not only in synthetic compounds and materials but also in a wide variety of natural products. Preparations of pyrroles bearing electron-withdrawing acyl groups such as the Knorr syntheses or the Hantzsch syntheses were described more than a century ago.[4] The pyrrole-forming condensation reaction between azirines and carbonyl compounds was first reported in 1967 by Ohta and co-workers,[5] and the same principle was later adopted by other groups.[6] A recent study by Khlebnikov and co-workers[7] incorporates the iron-catalyzed isomerization of 5-alkoxyisoxazoles found by Auricchio[8] with a nickel-catalyzed condensation reaction. Additionally, vinyl azides were employed as azirine equivalents by Chiba and Narasaka.[9]

RESULTS AND DISCUSSION

The initial task was to identify a suitable metal catalyst that does not interfere with the photoisomerization and is stable under irradiation with the UV light required for the formation of intermediates **2**. A screening was performed with cheap and

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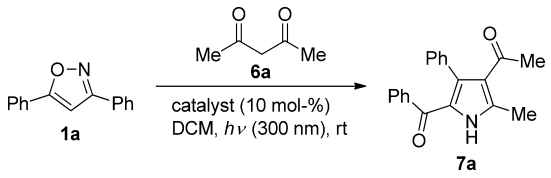
widely available first-row transition metal salts and complexes using LC/MS. They were selected for their ability to produce pyrrole **7a** from isoxazole **1a** and acetylacetone (**6a**) under irradiation with 300 nm UV light (Table 1).

Table 1. Catalyst Screening Using a Model Reaction

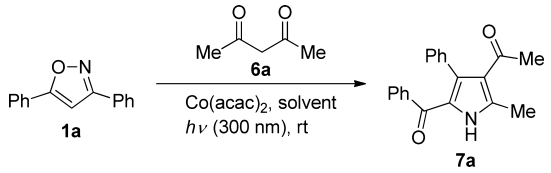


entry	catalyst	yield[a] (%)
1	none	0
2	$Mn(acac)_3$	57
3	$Mn(OAc)_3{\cdot}2H_2O$	nd[b]
4	$Fe(acac)_3$	nd[b]
5	**$Co(acac)_2$**	**83**[c]
6	$Co(acac)_3$	nd[b]
7	$CoCl_2$	37
8	$CoCl_2(dppf)$	nd[b]
9	$CoCl_2(PPh_3)_2$	nd[b]
10	$Co(hfacac)_2$	nd[b]
11	$Co(OAc)_2$	nd[b]
12	$Co(O^iPr)_2$	73
13	Co(salen)	nd[b]
14	$Co(SCN)_2$	63
15	$Ni(acac)_2{\cdot}xH_2O$	74
16	$NiCl_2$	nd[b]
17	$Ni(NH_3)_6Cl_2$	nd[b]
18	$Cu(MeCN)_4PF_6$	nd[b]
19	$Cu(NTf_2)_2$	nd[b]
20	$Cu(OAc)_2$	nd[b]
21	$(CuOTf)_2{\cdot}C_6H_6$	nd[b]

[a]Isolated yields after chromatography. [b]Not determined; low yield as judged by LC/MS. [c]When the experiment was performed in a pyrex tube instead of a quartz tube, the yield was 79%.

In the absence of a metal catalyst, no pyrrole formation was observed. Therefore, a de-Mayo-type photoreaction between the enol of acetylacetone and the azirine can be excluded. Furthermore, no reaction was detetcted when the isoxazole/diketone mixture was stirred in the presence of $Co(acac)_2$ in the dark. Thus, a cobalt-catalyzed condensation reaction between the isoxazole itself and acetylacetone can be ruled out. Significant catalytic activity was found for the acetylacetonato complexes of Mn^{III}, Co^{II}, or Ni^{II}, with $Co(acac)_2$ giving the highest yield of all screened compounds. Slightly lower yields can be obtained using $Co(SCN)_2$ and $Co(O^iPr)_2$, while it can be assumed that $Co(acac)_2$ is formed *in situ* from both precursors. Cobalt compounds with phosphine ligands or chelating ligands proved to be ineffective, the same applied to $Co^{III}(acac)_3$. A condensation reaction catalyzed by only base can also be excluded as no pyrrole formation could be detected if the corresponding azirine **2a** was stirred with acetylacetone and DBU (20 mol %) at room temperature in dichloromethane, whereas an almost quantitative yield was obtained using $Co(acac)_2$ (10 mol %). Thus, it is evident that the one-pot photoreaction is advantageous as the isolated yield of azirine **2a** was limited to ~50% in our hands in an earlier study (*vide supra*).[2] The structure of the product could be unambiguously determined by NMR spectroscopy and X-ray crystallography

Table 2. Screening of the Solvent and Catalyst Loading



entry	catalyst loading (mol %)	solvent	yield[a] (%)
1	10	MeOH	61
2	10	MeCN	64
3	10	DCM	83
4	5	DCM	31
5	20	DCM	87

[a]Isolated yields after chromatography.

(see the Supporting Information for details). With $Co(acac)_2$ as the optimal catalyst, we screened the solvent as well as the catalyst loading (Table 2).

Methanol and acetonitrile turned out to be inferior as solvents compared to dichloromethane. Dichloromethane is furthermore advantageous because of the often limited solubility of diarylisoxazoles in acetonitrile, which is a common solvent for photoreactions due to the broad spectral window. Lowering of the initial catalyst loading to 5 mol % resulted in a drastically reduced yield, while the use of 20 mol % instead of 10 mol % catalyst did not lead to a significant increase in the isolated yield. Using the optimized conditions, different isoxazoles **1** were reacted to give the corresponding tetrasubstituted pyrroles **7** (Table 3).[10]

The replacement of a phenyl group in position 3 on the isoxazole with a methyl substituent leads to lower yields; the same observation was made for a naphthyl group (entries 2 and 3). In the latter case, the photochemical ring enlargement appears to be too fast and the corresponding oxazole byproduct is being formed in spite of the reaction being performed in a one-pot fashion. A *p*-fluorophenyl group is tolerated well (entry 4). The introduction of a *p*-methoxy group (at the 3-phenyl substituent) results in a poor yield, whereas an excellent yield was obtained for the *p*-methoxycarbonyl derivative (entries 5 and 6). This is in accordance with a putative mechanism consisting of the nucleophilic addition to the C=N bond of the azirine, which is discussed below. The reaction failed with *o*-nitro groups (entry 7), while an *m*-nitro substituent was tolerated (entry 8). The phenyl group can also be replaced with a furyl or thienyl group (entry 9 or 10, respectively). The incorporation of additional electron-donating groups into the R^1 substituent gave high yields (entries 11 and 12) in contrast to the observations made for the R^2 group. A low yield was observed for an isoxazole with an R^1 alkyl group (entry 13), whereas the monosubstituted commercially available isoxazole **1o** was reacted in high yield (entry 14). In general, at least one aryl group, preferably as R^1, is required in this synthetic protocol to allow the initial photoisomerization in this particular setting.

The exclusion of oxygen during the reaction turned out to be essential as stable cobalt(III) complexes **8a–c** could be isolated and characterized if the photoreaction was conducted in the presence of air (Figure 1). The integrity of the complex in solution was checked by DOSY NMR spectroscopy. As in the case of $Co(acac)_3$, complex **8a** turned out to be catalytically inactive and very stable even toward concentrated hydrochloric acid at room temperature.

Next, we found that $Co(acac)_2$ as a catalyst can be replaced by mixtures of cobalt(II) chloride and potassium *tert*-butoxide.

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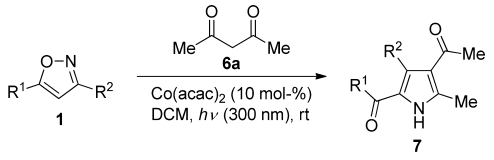
Table 3. Photochemical Cobalt-Catalyzed One-Pot Synthesis of Pyrroles from Isoxazoles



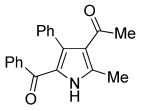
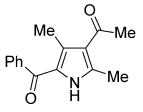
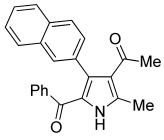
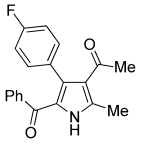
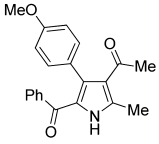
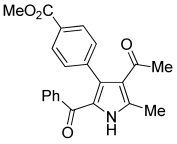
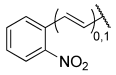
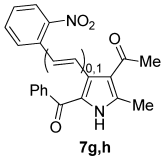
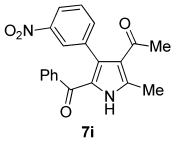
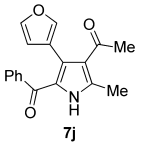
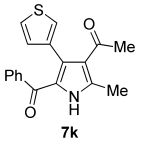
Entry	Isoxazole	R^1	R^2	Product	Yield[a]
1	**1a**	Ph	Ph	 **7a**	83%
2	**1b**	Ph	Me	 **7b**	56%
3	**1c**	Ph	2-naphthyl	 **7c**	41%
4	**1d**	Ph	*p*-C_6H_4-F	 **7d**	94%
5	**1e**	Ph	*p*-C_6H_4-OMe	 **7e**	30%
6	**1f**	Ph	*p*-C_6H_4-CO_2Me	 **7f**	92%
7	**1g,h**	Ph		 **7g,h**	–
8	**1i**	Ph	*m*-C_6H_4-NO_2	 **7i**	63%
9	**1j**	Ph	2-furyl	 **7j**	70%
10	**1k**	Ph	2-thienyl	 **7k**	63%

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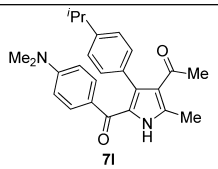
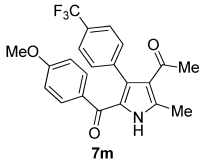
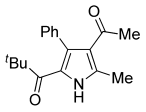
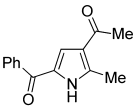
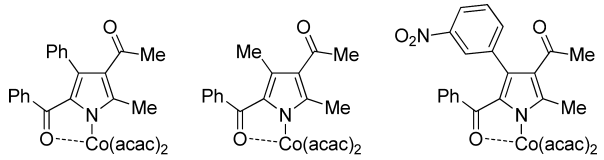
Table 3. continued

Entry	Isoxazole	R^1	R^2	Product	Yield[a]
11	**1l**	*p*-C_6H_4-NMe_2	*p*-C_6H_4-^{i}Pr	 **7l**	84%
12	**1m**	*p*-C_6H_4-OMe	*p*-C_6H_4-CF_3	 **7m**	92%
13	**1n**	^{t}Bu	Ph	 **7n**	29%[b]
14	**1o**	Ph	H	 **7o**	85%

[a]Isolated yields after chromatography. [b]Incomplete isoxazole consumption, with a yield (brsm) of 84%.

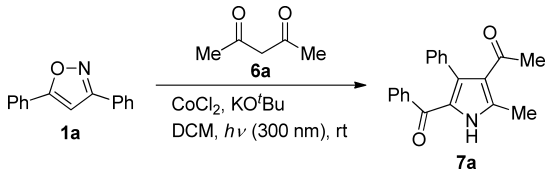


8a **8b** **8c**

Figure 1. Structures of the cobalt(III) complexes isolated as byproducts.

The molar ratio of $CoCl_2$ and KO^{t}Bu turned out to be crucial in this case; significant product formation could be observed only for a ratio of 1:2, while complex mixtures were obtained for 1:1 and 1:4 stoichiometries (Table 4; see the Supporting Information for LC/MS traces).

Table 4. Replacement of $Co(acac)_2$ with an Alternative Catalyst System



entry	$CoCl_2$ (mol %)	KO^{t}Bu (mol %)	molar ratio	yield[a] (%)
1	10	10	1:1	nd[b]
2	10	20	1:2	80
3	10	40	1:4	nd[b]

[a]Isolated yields after chromatography. [b]Not determined; low yield as judged by LC/MS.

Thus, $Co(acac)_2$ can be replaced with $CoCl_2$/KO^{t}Bu (1:2 molar ratio) without a significant loss of yield.

However, the $CoCl_2$/KO^{t}Bu mixture does not catalyze the reaction of azirines **2** with other 1,3-diketones such as 3,5-heptanedione (**6b**) or dibenzoylmethane (**6c**). $Co(acac)_2$ is not suitable as a catalyst as the acetylacetonato ligands would also be incorporated into the final pyrrole instead of the added 1,3-diketone, leading to the formation of product mixtures. The extension of the substrate spectrum could finally be accomplished using $Co(O^iPr)_2$ as a catalyst (Scheme 2).

Using this catalyst, alkyl or aryl groups can be used for R^3. The structure of pyrrole **7q** could be confirmed by X-ray crystallography (see the Supporting Information). When the unsymmetrical diketone benzoylacetone (**6d**) was employed, a 84:16 regioisomeric mixture of pyrroles **7r** and **7s** was isolated. As expected, the preferred pathway is the cyclization via the more reactive acetyl group (compared to the benzoyl group).

A plausible mechanism for this reaction would include the coordination of the metal catalyst to the nitrogen atom of the azirine (Scheme 3) and possibly the additional formation of a chelate ring involving the neighboring carbonyl oxygen atom.

A nucleophilic attack of anion **9** (which may also be bound to a metal center) at the C=N bond of the azirine **1** would form intermediate **10**. Anion **10** could then in turn form bicyclic system **11** as already suggested by Khlebnikov and co-workers.[6b,7] Alternatively, anion **10** could tautomerize to enolate **12**, which is prone to ring opening, yielding anion **13**. Either intermediate **11** or **13** could finally form pyrrole **7**.

If a solution of $Co(acac)_2$ in MeCN was directly infused into an ESI-MS source, a dominant species with an ion at m/z 415 could be observed (base peak), corresponding to $Co^{II}_2(acac)_3^+$. The dimer $Co^{II}_4(acac)_6^{2+}$ could be ruled out on the basis of the structure of the isotopic pattern [cobalt(II) acetylacetonate is known to have a tetrameric structure at least in the solid state].[11] Upon addition of azirine **2a** as well as acetylacetone (**6a**) to the mixture, a number of new peaks emerged, the strongest one being found at m/z 479 corresponding to cation **14** or **15** (Figure 2).

Isolation and fragmentation of the ion at m/z 479 yield mainly the ion at m/z 379, corresponding to cation **16** or **17** formed by extrusion of acetylacetone. Finally, MS/MS of the ion at m/z 379 produces the ion at m/z 280, corresponding to cation **18**, formed by abstraction of an acetylacetonyl radical with accompanying reduction of Co^{II} to Co^{I} (see the

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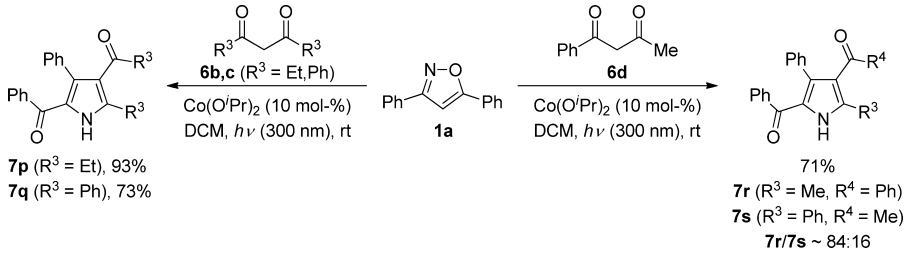
Scheme 2. Pyrrole Synthesis Using Non-acetylacetone Diketones



Scheme 3. Plausible Mechanism for Pyrrole Formation

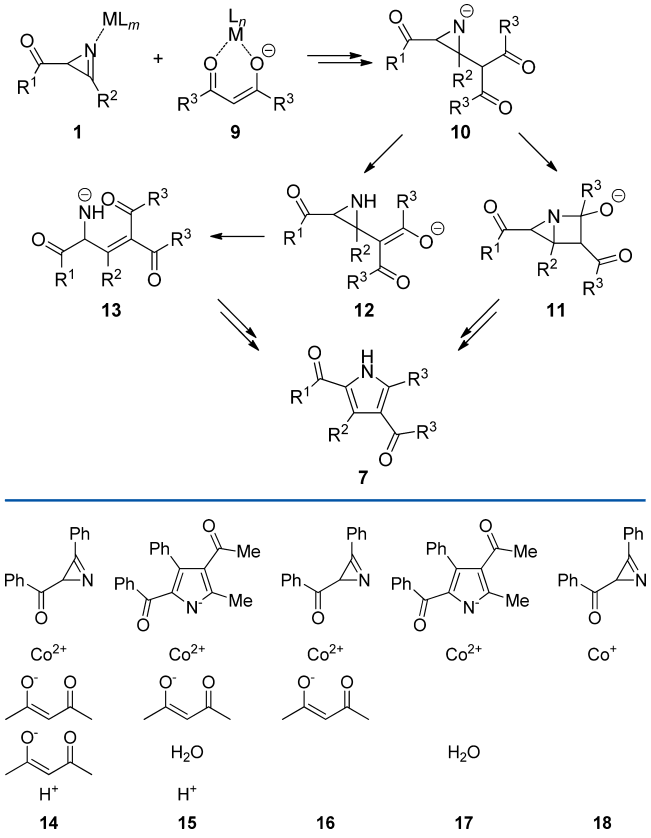


Figure 2. Putative cations observed during an ESI-MS experiment (for the sake of simplicity, separate constituents are shown).

Supporting Information for mass spectra). Evidently, the conditions inside an ESI source strongly deviate from the conditions applied in synthesis, but the observed ions and the fragmentation pathway at least suggest a coordination of cobalt to the azirine, thus enhancing the electrophilicity of the C=N moiety.

CONCLUSION

2,4-Diacylpyrroles could be synthesized from isoxazoles and acetylacetone in a photochemical one-pot procedure via azirines generated *in situ* and a subsequent $Co(acac)_2$- or $CoCl_2/KO^tBu$-catalyzed ring expansion reaction. The synthetic protocol can be extended to different 1,3-diketones when $Co(O^iPr)_2$ is used as a catalyst. The formation of catalytically inactive pyrrolato–cobalt(III) complexes could be observed in the presence of air.

EXPERIMENTAL SECTION

General Information. Anhydrous acetonitrile and dichloromethane were distilled from CaH_2 under nitrogen. Solvents were degassed using freeze–pump–thaw cycles or by nitrogen bubbling and an ultrasonic bath. $CDCl_3$ was stored over alumina (Brockmann activity grade I). All reagents were purchased from commercial suppliers and used without further purification. Photochemical reactions were performed in quartz tubes using a Rayonet photochemical reactor equipped with a circular array of 16 UV lamps (λ_{max} ~ 300 nm, 8 W each), a magnetic stirrer, and a cooling fan. TLC was conducted on silica gel 60 F_{254} plates (UV visualization). Preparative normal-phase chromatography was performed on silica gel (35–70 μm). Preparative reversed-phase chromatography was conducted using an ACE5-C_{18}PFP column (pore size of 5 μm, length of 15 cm, diameter of 30 mm) using a total flow rate of 37.5 mL min^{-1}. Melting points were determined in open capillary tubes. NMR spectra were recorded with 300, 400, and 600 MHz instruments using standard pulse sequences. The chemical shifts are given in parts per million (downfield relative to TMS) and were referenced to the residual solvent signal (δ_H = 7.26 ppm; δ_C = 77.16 ppm) or an external standard (α,α,α-trifluorotoluene in $CDCl_3$; δ_F = −63.9 ppm). IR spectra were recorded using a diamond ATR unit; wavenumbers are given in inverse centimeters. ESI-MS and ESI-HRMS spectra (given, m/z values) were recorded using an ion trap and an Q-ToF instrument with dual source and suitable external calibrant, respectively.

Isoxazole Synthesis. Compounds **1a**,[3b] **1b**,[12] **1n**,[13] and **2a**[2,3] were prepared as previously reported. Compound **1o** was purchased from a commercial supplier. Compounds **1c–m** were prepared according to the general procedure by Fokin and co-workers[14] from the corresponding aldehyde and alkyne precursors.

*3-(Naphthalen-2-yl)-5-phenyl-1,2-oxazole (**1c**).* Purification by flash chromatography (silica gel, 10:1 cyclohexane/ethyl acetate). Colorless solid (768 mg, 34%). R_f = 0.25 (20:1 cyclohexane/ethyl acetate). Mp: 145.6–146.7 °C. IR (ATR): 3118, 3053, 1572, 1496, 1449, 1408, 949, 907, 866, 828, 813, 763, 748, 691. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34–8.31 (m, 1H), 8.03 (dd, J = 8.5, 1.7 Hz, 1H), 7.97–7.86 (m, 5H), 7.58–7.45 (m, 5H), 6.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 163.2, 134.2, 133.4, 130.4, 129.2, 128.9, 128.6, 128.0, 127.6, 127.2, 126.8, 126.71, 126.67, 126.0, 124.1, 97.7. MS (ESI): m/z 272.0 $[M + H]^+$. Analytical data in accordance with the literature.[15]

*3-(4-Fluorophenyl)-5-phenyl-1,2-oxazole (**1d**).* Purification by flash chromatography (silica gel, 10:1 cyclohexane/ethyl acetate). Colorless solid (109 mg, 48%). R_f = 0.53 (5:1 cyclohexane/ethyl acetate). Mp: 167.4–168.3 °C. IR (ATR): 1606, 1527, 1493, 1448, 1430, 1231, 951, 845, 816, 765, 694. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.81 (m, 4H), 7.53–7.43 (m, 3H), 7.21–7.14 (m, 2H), 6.79 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 164.0 (d, J = 250.0 Hz), 162.2, 130.5, 129.2, 128.9 (d, J = 8.2 Hz), 127.5, 126.0, 125.5 (d, J = 3.1 Hz), 116.2 (d, J = 21.7 Hz), 97.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.7 (tt, J = 8.5, 5.2 Hz). MS (ESI): m/z 240.0 $[M + H]^+$. Analytical data in accordance with the literature.[16]

*3-(4-Methoxyphenyl)-5-phenyl-1,2-oxazole (**1e**).* Purification by flash chromatography (silica gel, 10:1 cyclohexane/ethyl acetate). Colorless solid (1.45 g, 58%). R_f = 0.28 (10:1 cyclohexane/ethyl acetate). Mp: 120.0–121.3 °C. IR (ATR): 1612, 1529, 1493, 1448, 1429, 1252, 1178, 1031, 837, 808, 763, 686. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–7.78 (m, 4H), 7.52–7.42 (m, 3H), 7.04–6.97 (m, 2H), 6.78 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 162.7, 161.2, 130.3, 129.1, 128.4, 127.7, 126.0, 121.8, 114.5, 97.4, 55.5. MS (ESI): m/z 252.0 $[M + H]^+$. Analytical data in accordance with the literature.[15,16b]

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*3-[4-(Methoxycarbonyl)phenyl]-5-phenyl-1,2-oxazole (**1f**).* Purification by flash chromatography (silica gel, 10:1 cyclohexane/ethyl acetate). Colorless solid (768 mg, 28%). R_f = 0.48 (5:1 cyclohexane/ethyl acetate). Mp: 195.0−195.9 °C. IR (ATR): 1716, 1449, 1279, 1114, 864, 767, 693. ^{1}H NMR, COSY (400 MHz, $CDCl_3$): δ 8.18−8.14 (m, 2H, $H^{3'/5'}$), 7.98−7.93 (m, 2H, $H^{2''/6''}$), 7.87−7.83 (m, 2H, $H^{2''/6''}$), 7.54−7.45 (m, 3H, $H^{3''/5''}$, $H^{4''}$), 6.88 (s, 1H, H^4), 3.96 (s, 3H, CH_3). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 171.1 (C^5), 166.7 (CO_2CH_3), 162.3 (C^3), 133.5 ($C^{1'}$), 131.6 ($C^{4'}$), 130.6 ($C^{4''}$), 130.4 ($C^{3'/5'}$), 129.2 ($C^{3''/5''}$), 127.4 ($C^{1''}$), 126.9 ($C^{2'/6'}$), 126.0 ($C^{2''/6''}$), 97.7 (C^4), 52.5 (CH_3). MS (ESI): m/z 280.1 $[M + H]^+$. HRMS (ESI): calcd for $C_{17}H_{14}NO_3^+$ 280.0974, found 280.0974.

*3-(2-Nitrophenyl)-5-phenyl-1,2-oxazole (**1g**).* Purification by flash chromatography (silica gel, 10:1 cyclohexane/ethyl acetate). Yellow solid (544 mg, 32%). R_f = 0.50 (10:3 cyclohexane/ethyl acetate). Mp: 89.7−90.5 °C. IR (ATR): 1572, 1529, 1451, 1403, 1351, 766, 690. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00−7.96 (m, 1H), 7.83−7.77 (m, 2H), 7.77−7.66 (m, 2H), 7.66−7.59 (m, 1H), 7.51−7.42 (m, 3H), 6.63 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 160.4, 148.7, 133.1, 131.7, 130.8, 130.6, 129.1, 127.1, 126.0, 124.6, 124.3, 99.7. MS (ESI): m/z 267.0 $[M + H]^+$. Analytical data in accordance with the literature.[17]

*3-[(E)-2-(2-Nitrophenyl)ethenyl]-5-phenyl-1,2-oxazole (**1h**).* Purification by flash chromatography (silica gel, 5:1 cyclohexane/ethyl acetate). Yellow solid (421 mg, 14%). R_f = 0.51 (5:3 cyclohexane/ethyl acetate). Mp: 134.2−135.5 °C. IR (ATR): 1573, 1534, 1495, 1437, 1357, 962, 928, 777, 763, 743, 684. ^{1}H NMR, COSY (400 MHz, $CDCl_3$): δ 8.04−7.99 (m, 1H, $H^{3''}$), 7.84−7.75 (m, 3H, $H^{6''}$, $H^{2''/6''}$), 7.72 (d, J = 16.4 Hz, 1H, $H^{2'}$), 7.68−7.61 (m, 1H, $H^{5''}$), 7.52−7.41 (m, 4H, $H^{4'}$, $H^{3''/5''}$, $H^{4''}$), 7.16 (d, J = 16.4 Hz, 1H, $H^{1'}$), 6.80 (s, 1H, H^4). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 170.3 (C^5), 162.0 (C^3), 148.1 ($C^{2''}$), 133.6 ($C^{5''}$), 131.7 ($C^{1''}$), 130.9 ($C^{2'}$), 130.5 ($C^{4''}$), 129.3 ($C^{4''}$), 129.1 ($C^{3''/5''}$), 128.6 ($C^{6''}$), 127.2 ($C^{1''}$), 125.9 ($C^{2''/6''}$), 125.0 ($C^{3''}$), 121.3 ($C^{1'}$), 96.7 (C^4). MS (ESI): m/z 293.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{17}H_{13}N_2O_3^+$ 293.0926, found 293.0922.

*3-(3-Nitrophenyl)-5-phenyl-1,2-oxazole (**1i**).* Purification by flash chromatography (silica gel, 10:1 cyclohexane/ethyl acetate). Yellow solid (382 mg, 22%). R_f = 0.53 (10:3 cyclohexane/ethyl acetate). Mp: 179.3−180.0 °C. IR (ATR): 1571, 1532, 1505, 1348, 807, 766, 740, 688. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69−8.67 (m, 1H), 8.32 (dd, J = 8.2, 2.3, 1.1 Hz, 1H), 8.25 (ddd, J = 7.8, 1.6, 1.1 Hz, 1H), 7.89−7.82 (m, 2H), 7.68 (pseudo-t, J = 8.0 Hz, 1H), 7.55−7.45 (m, 3H), 6.92 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 161.3, 148.8, 132.6, 131.1, 130.8, 130.2, 129.3, 127.1, 126.1, 124.8, 122.0, 97.4. MS (ESI): m/z 267.0 $[M + H]^+$. Analytical data in accordance with the literature.[18]

*3-(Furan-2-yl)-5-phenyl-1,2-oxazole (**1j**).* Purification by flash chromatography (silica gel, 20:1 cyclohexane/ethyl acetate). Colorless solid (388 mg, 19%). R_f = 0.24 (20:1 cyclohexane/ethyl acetate). Mp: 96.0−97.5 °C. IR (ATR): 1616, 1570, 1508, 1453, 1436, 1016, 970, 885, 810, 765, 687, 670. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87−7.80 (m, 2H), 7.59−7.56 (m, 1H), 7.53−7.42 (m, 3H), 6.99−6.94 (m, 1H), 6.79 (s, 1H), 6.58−6.53 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 155.5, 144.5, 144.0, 130.5, 129.2, 127.3, 126.0, 111.9, 110.3, 97.1. MS (ESI): m/z 212.0 $[M + H]^+$. Analytical data in accordance with the literature.[19]

*5-Phenyl-3-(thiophen-2-yl)-1,2-oxazole (**1k**).* Purification by flash chromatography (silica gel, 30:1 cyclohexane/ethyl acetate). Colorless solid (668 mg, 29%). R_f = 0.22 (30:1 cyclohexane/ethyl acetate). Mp: 107.5−108.4 °C. IR (ATR): 1614, 1592, 1576, 1491, 1447, 1432, 1394, 910, 848, 804, 763, 712, 685. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87−7.79 (m, 2H), 7.55−7.42 (m, 5H), 7.17−7.12 (m, 1H), 6.76 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 158.3, 131.0, 130.5, 129.2, 127.8, 127.7, 127.4, 126.0, 97.6. MS (ESI): m/z 227.9 $[M + H]^+$. Analytical data in accordance with the literature.[20]

*5-(N,N-Dimethylphenyl)-3-[4-(propan-2-yl)phenyl]-1,2-oxazole (**1l**).* Purification by flash chromatography (silica gel, 10:1 cyclohexane/ethyl acetate). Colorless solid (198 mg, 32%). R_f = 0.41 (5:1 cyclohexane/ethyl acetate). Mp: 141.0−141.8 °C. IR (ATR): 2959, 1615, 1517, 1438, 1373, 1194, 951, 839, 818, 795. ^{1}H NMR, COSY (400 MHz, $CDCl_3$): δ 7.81−7.77 (m, 2H, $H^{2''/6''}$), 7.73−7.68 (m, 2H, $H^{2''/6''}$), 7.35−7.31 (m, 2H, $H^{3'/5'}$), 6.78−6.73 (m, 2H, $H^{3''/5''}$), 6.60 (s, 1H, H^4), 3.04 [s, 6H, $N(CH_3)_2$], 2.97 [septet, J = 6.9 Hz, $CH(CH_3)_2$], 1.29 [d, J = 6.9 Hz, $CH(CH_3)_2$]. ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 171.2 (C^5), 162.9 (C^3), 151.5 ($C^{4''}$), 150.9 ($C^{4'}$), 127.3 ($C^{1'}$), 127.2 ($C^{2''/6''}$), 127.1 ($C^{3'/5'}$), 126.9 ($C^{2'/6'}$), 115.7 ($C^{1''}$), 112.0 ($C^{3''/5''}$), 94.8 (C^4), 40.4 [$N(CH_3)_2$], 34.2 [$CH(CH_3)_2$], 24.0 [$CH(CH_3)_2$]. MS (ESI): m/z 307.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{20}H_{23}N_2O^+$ 307.1810, found 307.1797.

*5-(4-Methoxyphenyl)-3-[4-(trifluoromethyl)phenyl]-1,2-oxazole (**1m**).* Purification by flash chromatography (silica gel, 40:1 cyclohexane/ethyl acetate). Colorless solid (156 mg, 68%). R_f = 0.33 (10:1 cyclohexane/ethyl acetate). Mp: 192.1−193.2 °C. IR (ATR): 1616, 1508, 1439, 1323, 1256, 1167, 1113, 1065, 1030, 951, 841, 808. ^{1}H NMR, COSY (600 MHz, $CDCl_3$): δ 8.01−7.97 (m, 2H, $H^{2'/6'}$), 7.81−7.77 (m, 2H, $H^{2''/6''}$), 7.77−7.72 (m, 2H, $H^{3'/5'}$), 7.04−6.99 (m, 2H, $H^{3''/5''}$), 6.75 (s, 1H, H^4), 3.88 (s, 3H, CH_3). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$): δ 171.2 (C^5), 161.9 (C^3), 161.5 ($C^{4''}$), 132.9 ($C^{1'}$), 131.9 (q, J = 32.8 Hz, $C^{4'}$), 127.7 ($C^{2''/6''}$), 127.3 ($C^{2'/6'}$), 126.1 (q, J = 3.6 Hz, $C^{3'/5'}$), 124.0 (q, J = 271.9 Hz, CF_3), 120.1 ($C^{1''}$), 114.6 ($C^{3''/5''}$), 96.2 (C^4), 55.6 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ −64.0 (s, CF_3). MS (ESI): m/z 320.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{17}H_{13}F_3NO_2^+$ 320.0898, found 320.0898.

Pyrrole Synthesis. *General Procedure A.* To an oven-dried quartz tube under a nitrogen atmosphere were added the corresponding isoxazole **1**, acetylacetone (**6a**, 1.10 equiv), $Co(acac)_2$ (0.10 equiv), and dry dichloromethane (20 mL). The solution was degassed and irradiated (300 nm, 16 × 8 W). After TLC or LC/MS analysis indicated consumption of the starting material, the solvent was removed *in vacuo* and the residue was purified by flash chromatography (silica gel, 98:2 → 60:40 cyclohexane/ethyl acetate).

General Procedure B. To an oven-dried quartz tube under a nitrogen atmosphere were added the corresponding isoxazole **1**, 1,3-diketone **6** (2.00 equiv), $Co(O^iPr)_2$ (0.10 equiv), and dry dichloromethane (20 mL). Otherwise identical to general procedure A.

*1-(5-Benzoyl-2-methyl-4-phenyl-1H-pyrrol-3-yl)ethanone (**7a**).* Following general procedure A, isoxazole **1a** (60.0 mg, 0.271 mmol) afforded the title compound (68.0 mg, 0.224 mmol, 83%) as a colorless solid. R_f = 0.31 (3:1 cyclohexane/ethyl acetate). Mp: 195.6−196.7 °C. IR (ATR): 3261, 1656, 1602, 1575, 1544, 1481, 1413, 1285, 918, 738, 697, 669. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 11.04 (br s, 1H, N*H*), 7.31−7.26 (m, 2H, $H^{2''/6''}$), 7.18−7.13 (m, 1H, $H^{4''}$), 7.09−6.95 (m, 7H, $H^{2''/6''}$, $H^{3''/5''}$, $H^{4''}$, $H^{3''/5''}$), 2.63 (s, 3H, $C^{2'}CH_3$), 1.81 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 197.3 (C^1), 188.0 (C^5CO), 140.9 ($C^{2'}$), 137.7 ($C^{1''}$), 134.7 ($C^{1''}$), 134.1 ($C^{4'}$), 131.0 ($C^{4''}$), 130.9 + 127.8 + 127.4 ($C^{2''/6''}$, $C^{3''/5''}$, $C^{3''/5''}$), 128.7 ($C^{2''/6''}$), 127.5 ($C^{4''}$), 127.0 ($C^{5'}$), 124.4 ($C^{3'}$), 30.8 (C^2), 14.4 ($C^{2'}CH_3$). MS (ESI): m/z 304.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{20}H_{18}NO_2^+$ 304.1338, found 304.1347. Crystals suitable for X-ray crystallography could be obtained by recrystallization of **7a** from cyclohexane/ethyl acetate (1:1).

If the irradiation was performed with 1.00 equiv of $Co(acac)_2$ in the presence of air, bis(acetylacetonato-κ^2O,O')-(1-{2-methyl-5-[(oxo-κO)-(phenyl)methyl]-4-phenyl-1*H*-pyrrol-3-yl-κN}ethanonato)cobalt(III) (**8a**, 34.9 mg, 62.3 μmol, 23%) could be isolated as a green lyophilizate after purification by preparative HPLC (60:40 MeCN/H_2O; t_R = 6.5−8.0 min). R_f = 0.24 (3:1 cyclohexane/ethyl acetate). IR (ATR): 1650, 1571, 1516, 1480, 1371, 1250, 1022, 931, 739, 701, 664, 636. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ 7.17−7.08 (m, 4H, $H^{4''}$, $H^{2''/6''}$, $H^{4''}$), 7.08−6.99 (m, 4H, $H^{2''/6''}$, $H^{3''/5''}$), 6.94−6.87 (m, 2H, $H^{3''/5''}$), 5.55 (s, 1H, CH^{acac}), 5.54 (s, 1H, CH^{acac}), 2.53 (s, 3H, $C^{2'}CH_3$), 2.26 (s, 3H, CH_3^{acac}), 2.16 (s, 3H, CH_3^{acac}), 2.11 (s, 3H, CH_3^{acac}), 2.10 (s, 3H, CH_3^{acac}), 1.83 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$): δ 197.1 (C^1), 194.6 ($C^{5'}CO$), 190.6 (CO^{acac}), 189.9 (CO^{acac}), 189.6 (CO^{acac}), 189.5 (CO^{acac}), 157.4 ($C^{2'}$), 142.7 + 139.5 ($C^{4'}$, $C^{5'}$), 135.5 ($C^{1''}$), 134.6 ($C^{1''}$), 130.6 ($C^{3''/5''}$), 130.4 ($C^{4''}$), 129.7 ($C^{3'}$), 128.8 ($C^{2''/6''}$), 127.8 ($C^{2''/6''}$), 127.4 ($C^{4''}$), 127.0 ($C^{3''/5''}$), 97.8 (CH^{acac}), 97.1 (CH^{acac}), 31.0 (C^2), 26.48 (CH_3^{acac}), 26.42 (CH_3^{acac}), 26.35 (CH_3^{acac}), 25.8 (CH_3^{acac}),

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13.6 ($C^{2\prime}CH_3$). MS (ESI): m/z 560.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{30}H_{30}CoNNaO_6^+$ 582.1303, found 582.1324.

*1-(5-Benzoyl-2,4-dimethyl-1H-pyrrol-3-yl)ethanone (**7b**).* Following general procedure A, isoxazole **1b** (43.1 mg, 0.271 mmol) afforded the title compound (36.4 mg, 0.151 mmol, 56%) as a colorless solid. R_f = 0.19 (3:1 cyclohexane/ethyl acetate). Mp: 140.6−141.5 °C. IR (ATR): 3264, 1600, 1548, 1506, 1415, 1285, 701. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 10.18 (br s, 1H, N*H*), 7.69−7.65 (m, 2H, $H^{2\prime\prime/6\prime\prime}$), 7.58−7.52 (m, 1H, $H^{4\prime\prime}$), 7.49−7.44 (m, 2H, $H^{3\prime\prime/5\prime\prime}$), 2.58 (s, 3H, $C^{2\prime}CH_3$), 2.44 (s, 3H, H^2), 2.16 (s, 3H, $C^{4\prime}CH_3$). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 195.6 (C^1), 187.6 ($C^{5\prime}CO$), 140.8 ($C^{2\prime}$), 139.5 ($C^{1\prime\prime}$), 132.0 ($C^{4\prime\prime}$), 130.4 ($C^{4\prime}$), 128.8 ($C^{2\prime\prime/6\prime\prime}$), 128.6 ($C^{3\prime\prime/5\prime\prime}$), 127.7 ($C^{5\prime}$), 124.4 ($C^{3\prime}$), 31.5 ($C^1$), 15.4 ($C^{2\prime}CH_3$), 14.6 ($C^{4\prime}CH_3$). MS (ESI): m/z 242.0 $[M + H]^+$. HRMS (ESI) calcd for $C_{15}H_{16}NO_2^+$ 242.1181, found 242.1171. Analytical data in accordance with the literature.[21]

If the irradiation was performed with 1.00 equiv of $Co(acac)_2$ in the presence of air, bis(acetylacetonato-κ^2O,O')-(1-{2,4-dimethyl-5-[(oxo-κO)(phenyl)methyl]-1*H*-pyrrol-3-yl-κN}ethanonato)cobalt(III) (**8b**, 20.2 mg, 40.7 μmol, 15%) could be isolated as a green lyophilizate after purification by preparative HPLC (45:55 MeCN/H_2O; t_R = 11.5−14.5 min). R_f = 0.14 (3:1 cyclohexane/ethyl acetate). IR (ATR): 1645, 1572, 1516, 1373, 1254, 1070, 1013, 938, 778, 716, 635. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ 7.62−7.59 (m, 2H, $H^{2\prime\prime/6\prime\prime}$), 7.52−7.48 (m, 1H, $H^{4\prime\prime}$), 7.44−7.39 (m, 2H, $H^{3\prime\prime/5\prime\prime}$), 5.524 (s, 1H, CH^{acac}), 5.517 (s, 1H, CH^{acac}), 2.50 (s, 3H, $C^{2\prime}CH_3$), 2.46 (s, 3H, H^2), 2.27 (s, 3H, $C^{4\prime}CH_3$), 2.25 (s, 3H, CH_3^{acac}), 2.13 (s, 3H, CH_3^{acac}), 2.09 (s, 3H, CH_3^{acac}), 2.07 (s, 3H, CH_3^{acac}). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$): δ 195.4 (C^1), 193.3 ($C^{5\prime}CO$), 190.7 (CO^{acac}), 189.9 (CO^{acac}), 189.6 (CO^{acac}), 189.4 (CO^{acac}), 158.6 ($C^{2\prime}$), 140.5 + 140.0 ($C^{4\prime}$, $C^{5\prime}$), 135.8 ($C^{1\prime\prime}$), 131.3 ($C^{4\prime\prime}$), 130.2 ($C^{3\prime}$), 129.0 ($C^{2\prime\prime/6\prime\prime}$), 128.1 ($C^{3\prime\prime/5\prime\prime}$), 97.9 ($CH^{acac}$), 97.2 ($CH^{acac}$), 31.7 ($C^2$), 26.54 ($CH_3^{acac}$), 26.44 ($CH_3^{acac}$), 26.41 ($CH_3^{acac}$), 25.9 ($CH_3^{acac}$), 15.0 ($C^{4\prime}CH_3$), 14.3 ($C^{2\prime}CH_3$). MS (ESI): m/z 498.0 $[M + H]^+$. HRMS (ESI) calcd for $C_{25}H_{28}CoNNaO_6^+$ 520.1146, found 520.1143.

*1-[5-Benzoyl-2-methyl-4-(naphthalen-2-yl)-1H-pyrrol-3-yl]-ethanone (**7c**).* Following general procedure A, isoxazole **1c** (73.5 mg, 0.271 mmol) afforded the title compound (39.1 mg, 0.111 mmol, 41%) as a colorless solid. R_f = 0.30 (3:1 cyclohexane/ethyl acetate). Mp: 180.5−181.6 °C. IR (ATR): 3262, 1601, 1544, 1414, 1284, 742, 697. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 10.31 (br s, 1H, N*H*), 7.74−7.69 (m, 1H, $H^{5\prime\prime}$), 7.58−7.53 (m, 2H, $H^{4\prime\prime}$), 7.46−7.36 (m, 3H, $H^{1\prime\prime}$, $H^{6\prime\prime}$, $H^{7\prime\prime}$), 7.27−7.22 (m, 2H, $H^{2\prime\prime\prime/6\prime\prime\prime}$), 7.20−7.15 (m, 1H, $H^{3\prime\prime}$), 6.87−6.82 (m, 1H, $H^{4\prime\prime\prime}$), 6.78−6.72 (m, 2H, $H^{3\prime\prime\prime/5\prime\prime\prime}$), 2.66 (s, 3H, $C^{2\prime}CH_3$), 1.83 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 197.3 (C^1), 187.9 ($C^{5\prime}CO$), 140.5 ($C^{2\prime}$), 137.7 ($C^{1\prime\prime\prime}$), 133.8 ($C^{4\prime}$), 132.7 ($C^{8a\prime\prime}$), 132.4 ($C^{4a\prime\prime}$), 132.0 ($C^{2\prime\prime}$), 130.7 ($C^{4\prime\prime\prime}$), 130.3 ($C^{1\prime\prime}$), 128.5 ($C^{3\prime\prime}$), 128.4 ($C^{2\prime\prime/6\prime\prime\prime}$), 127.8 + 127.5 ($C^{6\prime\prime}$, $C^{7\prime\prime}$), 127.6 ($C^{5\prime\prime}$), 127.3 ($C^{3\prime\prime\prime/5\prime\prime\prime}$), 126.3 + 126.2 ($C^{4\prime\prime}$, $C^{8\prime\prime}$), 124.5 ($C^{3\prime}$), 31.1 (C^2), 14.6 ($C^{2\prime}CH_3$). MS (ESI): m/z 354.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{24}H_{20}NO_2^+$ 354.1494, found 354.1483.

*1-[5-Benzoyl-4-(4-fluorophenyl)-2-methyl-1H-pyrrol-3-yl]-ethanone (**7d**).* Following general procedure A, isoxazole **1d** (53.6 mg, 0.224 mmol) afforded the title compound (67.7 mg, 0.211 mmol, 94%) as a colorless solid. R_f = 0.27 (3:1 cyclohexane/ethyl acetate). Mp: 181.6−182.4 °C. IR (ATR): 1655, 1599, 1522, 1479, 1415, 1275, 1222, 917, 843, 815, 745, 697, 667. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 10.68 (br s, 1H, N*H*), 7.28−7.20 (m, 3H, $H^{2\prime\prime\prime/6\prime\prime\prime}$, $H^{4\prime\prime\prime}$), 7.07−7.01 (m, 2H, $H^{3\prime\prime\prime/5\prime\prime\prime}$), 7.01−6.94 (m, 2H, $H^{2\prime\prime/6\prime\prime}$), 6.78−6.71 (m, 2H, $H^{3\prime\prime/5\prime\prime}$), 2.62 (s, 3H, $C^{2\prime}CH_3$), 1.84 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 197.0 (C^1), 187.9 ($C^{5\prime}CO$), 162.3 (d, J = 247.4 Hz, $C^{4\prime\prime}$), 140.8 ($C^{2\prime}$), 137.7 ($C^{1\prime\prime\prime}$), 132.7 ($C^{4\prime}$), 132.5 (d, J = 8.1 Hz, $C^{2\prime\prime/6\prime\prime}$), 131.2 ($C^{4\prime\prime\prime}$), 130.7 (d, J = 3.7 Hz, $C^{1\prime\prime}$), 128.7 ($C^{2\prime\prime/6\prime\prime\prime}$), 127.6 ($C^{3\prime\prime\prime/5\prime\prime\prime}$), 127.2 ($C^{5\prime}$), 124.5 ($C^{3\prime}$), 114.9 (d, J = 21.5 Hz, $C^{3\prime\prime/5\prime\prime}$), 31.0 ($C^2$), 14.5 ($C^{2\prime}CH_3$). ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.6 (tt, J = 8.6, 5.2 Hz, $F^{4\prime\prime}$). MS (ESI): m/z 322.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{20}H_{16}FNNaO_2^+$ 344.1063, found 344.1072.

*1-[5-Benzoyl-4-(4-methoxyphenyl)-2-methyl-1H-pyrrol-3-yl]-ethanone (**7e**).* Following general procedure A, isoxazole **1e** (68.1 mg, 0.271 mmol) afforded the title compound (26.0 mg, 80.0 μmol, 30%) as a colorless lyophilizate after purification by preparative HPLC (50:50 MeCN/H_2O; t_R = 5.2−6.7 min). R_f = 0.25 (3:1 cyclohexane/ethyl acetate). IR (ATR): 3262, 1604, 1574, 1525, 1482, 1418, 1286, 1246, 1178, 697. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 10.01 (br s, 1H, N*H*), 7.29−7.23 (m, 2H, $H^{2\prime\prime/6\prime\prime}$), 7.23−7.19 (m, 1H, $H^{4\prime\prime}$), 7.05−6.99 (m, 2H, $H^{3\prime\prime/5\prime\prime}$), 6.93−6.88 (m, 2H, $H^{2\prime\prime/6\prime\prime}$), 6.61−6.56 (m, 2H, $H^{3\prime\prime/5\prime\prime}$), 3.72 (s, 3H, OCH_3), 2.61 (s, 3H, $C^{2\prime}CH_3$), 1.85 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 197.4 (C^1), 187.7 ($C^{5\prime}CO$), 159.2 ($C^{4\prime\prime}$), 140.2 ($C^{2\prime}$), 137.8 ($C^{1\prime\prime\prime}$), 133.6 ($C^{4\prime}$), 132.0 ($C^{2\prime\prime/6\prime\prime}$), 130.9 ($C^{4\prime\prime\prime}$), 128.7 ($C^{2\prime\prime/6\prime\prime\prime}$), 127.5 ($C^{3\prime\prime\prime/5\prime\prime\prime}$), 127.0 ($C^{5\prime}$), 126.8 ($C^{1\prime\prime}$), 124.5 ($C^{3\prime}$), 113.5 ($C^{3\prime\prime/5\prime\prime}$), 55.4 ($OCH_3$), 30.9 ($C^2$), 14.6 ($C^{2\prime}CH_3$). MS (ESI): m/z 334.2 $[M + H]^+$. HRMS (ESI) calcd for $C_{21}H_{19}NNaO_3^+$ 356.1263, found 356.1272.

*1-{5-Benzoyl-4-[4-(methoxycarbonyl)phenyl]-2-methyl-1H-pyrrol-3-yl}ethanone (**7f**).* Following general procedure A, isoxazole **1f** (75.7 mg, 0.271 mmol) afforded the title compound (90.0 mg, 0.250 mmol, 92%) as a colorless solid. R_f = 0.21 (3:1 cyclohexane/ethyl acetate). Mp: 168.0−168.9 °C. IR (ATR): 3262, 1720, 1609, 1480, 1415, 1275, 1177, 1110, 918, 742, 700. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 10.93 (br s, 1H, N*H*), 7.75−7.66 (m, 2H, $H^{3\prime\prime/5\prime\prime}$), 7.31−7.21 (m, 2H, $H^{2\prime\prime\prime/6\prime\prime\prime}$), 7.21−7.12 (m, 1H, $H^{4\prime\prime\prime}$), 7.12−7.04 (m, 2H, $H^{2\prime\prime/6\prime\prime}$), 7.04−6.93 (m, 2H, $H^{3\prime\prime\prime/5\prime\prime\prime}$), 3.88 (s, 3H, CO_2CH_3), 2.62 (s, 3H, $C^{2\prime}CH_3$), 1.81 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 196.7 (C^1), 187.8 ($C^{5\prime}CO$), 166.8 (CO_2CH_3), 140.9 ($C^{2\prime}$), 139.9 ($C^{1\prime\prime}$), 137.5 ($C^{1\prime\prime\prime}$), 132.6 ($C^{4\prime}$), 131.4 ($C^{4\prime\prime\prime}$), 130.9 ($C^{2\prime\prime/6\prime\prime}$), 129.0 ($C^{4\prime\prime}$), 128.9 ($C^{3\prime\prime/5\prime\prime}$), 128.7 ($C^{2\prime\prime/6\prime\prime\prime}$), 127.6 ($C^{3\prime\prime\prime/5\prime\prime\prime}$), 127.0 ($C^{5\prime}$), 124.3 ($C^{3\prime}$), 52.3 ($CO_2CH_3$), 30.9 ($C^2$), 14.4 ($C^{2\prime}CH_3$). MS (ESI): m/z 362.2 $[M + H]^+$. HRMS (ESI) calcd for $C_{22}H_{19}NNaO_4^+$ 384.1212, found 384.1230.

*1-[5-Benzoyl-2-methyl-4-(3-nitrophenyl)-1H-pyrrol-3-yl]-ethanone (**7i**).* Following general procedure A, isoxazole **1i** (72.2 mg, 0.271 mmol) afforded the title compound (60.0 mg, 0.170 mmol, 63%) as a yellow solid. R_f = 0.15 (3:1 cyclohexane/ethyl acetate). Mp: 187.8−188.9 °C. IR (ATR): 3271, 1605, 1529, 1409, 1347, 1278, 1074, 939, 865, 732, 696, 664. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 10.65 (br s, 1H, N*H*), 7.92 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H, $H^{3\prime\prime}$), 7.82−7.80 (m, 1H, $H^{2\prime\prime}$), 7.45−7.40 (m, 1H, $H^{6\prime\prime}$), 7.31−7.21 (m, 3H, $H^{5\prime\prime}$, $H^{2\prime\prime/6\prime\prime}$), 7.19−7.14 (m, 1H, $H^{4\prime\prime\prime}$), 7.03−6.97 (m, 2H, $H^{3\prime\prime/5\prime\prime\prime}$), 2.66 (s, 3H, $C^{2\prime}CH_3$), 1.95 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 195.6 (C^1), 187.6 ($C^{5\prime}CO$), 147.4 ($C^{3\prime\prime}$), 140.8 ($C^{2\prime}$), 137.6 ($C^{1\prime\prime\prime}$), 136.7 ($C^{6\prime\prime}$), 136.5 ($C^{1\prime\prime}$), 131.3 ($C^{4\prime\prime\prime}$), 131.0 ($C^{4\prime}$), 128.7 ($C^{5\prime\prime}$), 128.4 ($C^{2\prime\prime/6\prime\prime\prime}$), 127.8 ($C^{3\prime\prime/5\prime\prime\prime}$), 127.5 ($C^{5\prime}$), 125.9 ($C^{1\prime\prime}$), 124.0 ($C^{3\prime}$), 122.3 ($C^{4\prime\prime}$), 31.2 ($C^2$), 14.7 ($C^{2\prime}CH_3$). MS (ESI): m/z 349.2 $[M + H]^+$. HRMS (ESI) calcd for $C_{20}H_{16}N_2NaO_4^+$ 371.1008, found 371.0999.

If the irradiation was performed with 1.00 equiv of $Co(acac)_2$ in the presence of air, bis(acetylacetonato-κ^2O,O')-(1-{2-methyl-4-(3-nitrophenyl)-5-[(oxo-κO)(phenyl)methyl]-1*H*-pyrrol-3-yl-κN}-ethanonato)cobalt(III) (**8c**, 26.2 mg, 43.4 μmol, 16%) could be isolated as a green lyophilizate after purification by preparative HPLC (45:55 MeCN/H_2O; t_R = 3.0−4.5 min). R_f = 0.13 (3:1 cyclohexane/ethyl acetate). IR (ATR): 1654, 1573, 1519, 1473, 1411, 1373, 1347, 1252, 939, 701. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 7.98−7.93 (m, 1H, $H^{4\prime\prime}$), 7.80−7.75 (m, 1H, $H^{2\prime\prime}$), 7.49−7.42 (m, 1H, $H^{6\prime\prime}$), 7.34−7.26 (m, 1H, $H^{5\prime\prime}$), 7.15−7.10 (m, 1H, $H^{4\prime\prime\prime}$), 7.10−7.06 (m, 2H, $H^{2\prime\prime/6\prime\prime\prime}$), 6.95−6.89 (m, 2H, $H^{3\prime\prime/5\prime\prime\prime}$), 5.57 (s, 1H, CH^{acac}), 5.56 (s, 1H, CH^{acac}), 2.52 (s, 3H, $C^{2\prime}CH_3$), 2.27 (s, 3H, CH_3^{acac}), 2.16 (s, 3H, CH_3^{acac}), 2.14 (br s, 6H, 2 × CH_3^{acac}), 1.91 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 195.8 (C^1), 195.4 ($C^{5\prime}CO$), 190.9 (CO^{acac}), 190.0 (CO^{acac}), 189.8 (CO^{acac}), 189.6 (CO^{acac}), 157.3 ($C^{2\prime}$), 147.5 ($C^{3\prime\prime}$), 139.8 ($C^{5\prime}$), 138.9 ($C^{4\prime}$), 137.3 ($C^{1\prime\prime}$), 136.6 ($C^{6\prime\prime}$), 134.5 ($C^{1\prime\prime\prime}$), 130.7 ($C^{4\prime\prime\prime}$), 129.7 ($C^{3\prime}$), 128.6 ($C^{5\prime\prime}$), 128.5 ($C^{2\prime\prime/6\prime\prime\prime}$), 127.4 ($C^{3\prime\prime/5\prime\prime\prime}$), 125.6 ($C^{2\prime\prime}$), 122.2 ($C^{4\prime\prime}$), 97.9 ($CH^{acac}$), 97.1 ($CH^{acac}$), 31.4 ($C^2$), 26.5 ($CH_3^{acac}$), 26.4 (2 × CH_3^{acac}), 25.8 (CH_3^{acac}), 13.7 ($C^{2\prime}CH_3$). MS (ESI): m/z 605.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{30}H_{30}CoN_2O_8^+$ 605.1334, found 605.1333.

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*1-[5-Benzoyl-4-(furan-3-yl)-2-methyl-1H-pyrrol-3-yl]ethanone (**7j**).* Following general procedure A, isoxazole **1j** (57.2 mg, 0.271 mmol) afforded the title compound (56.2 mg, 0.190 mmol, 70%) as a colorless solid. R_f = 0.33 (3:1 cyclohexane/ethyl acetate). Mp: 150.9−151.7 °C. IR (ATR): 3263, 1618, 1544, 1479, 1407, 1283, 1181, 941, 740, 697, 665. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 11.05 (br s, 1H, N*H*), 7.47−7.43 (m, 2H, $H^{2'''/6'''}$), 7.35−7.29 (m, 2H, $H^{4''}$, $H^{4'''}$), 7.23−7.17 (m, 2H, $H^{3'''/5'''}$), 6.04 (dd, J = 3.3, 1.8 Hz, 1H, $H^{3''}$), 5.86 (dd, J = 3.3, 0.8 Hz, 1H, $H^{2''}$), 2.65 (s, 3H, $C^{2'}CH_3$), 1.96 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 196.3 (C^1), 187.7 ($C^{5'}CO$), 145.3 ($C^{1''}$), 142.1 ($C^{4''}$), 141.4 ($C^{2'}$), 138.1 ($C^{1'''}$), 131.5 ($C^{4'''}$), 128.4 ($C^{2'''/6'''}$), 128.2 ($C^{5'}$), 127.8 ($C^{3'''/5'''}$), 123.9 ($C^{3'}$), 121.9 ($C^{4'}$), 112.6 ($C^{2''}$), 111.4 ($C^{3''}$), 29.1 (C^2), 14.6 ($C^{2'}CH_3$). MS (ESI): m/z 294.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{18}H_{15}NNaO_3^+$ 316.0950, found 316.0963.

*1-[5-Benzoyl-2-methyl-4-(thiophen-3-yl)-1H-pyrrol-3-yl]-ethanone (**7k**).* Following general procedure A, isoxazole **1k** (61.6 mg, 0.271 mmol) afforded the title compound (52.3 mg, 0.170 mmol, 63%) as a colorless solid. R_f = 0.36 (3:1 cyclohexane/ethyl acetate). Mp: 163.8−164.8 °C. IR (ATR): 3248, 1656, 1600, 1573, 1534, 1480, 1428, 1282, 736, 694, 665. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 10.88 (br s, 1H, N*H*), 7.46−7.41 (m, 2H, $H^{2'''/6'''}$), 7.30−7.24 (m, 1H, $H^{4'''}$), 7.14−7.08 (m, 3H, $H^{4''}$, $H^{3'''/5'''}$), 6.72 (dd, J = 4.9, 3.5 Hz, 1H, $H^{3''}$), 6.70 (d, J = 3.5, 1.4 Hz, 1H, $H^{2''}$), 2.61 (s, 3H, $C^{2'}CH_3$), 1.96 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 197.1 (C^1), 187.9 ($C^{5'}CO$), 140.7 ($C^{2'}$), 137.9 ($C^{1'''}$), 135.0 ($C^{4'}$), 131.3 ($C^{4'''}$), 129.9 ($C^{2''}$), 128.4 ($C^{2'''/6'''}$), 128.1 ($C^{5'}$), 127.6 ($C^{3'''/5'''}$), 127.4 ($C^{4''}$), 126.9 ($C^{3''}$), 125.2 ($C^{3'}$), 124.8 ($C^{1''}$), 30.2 (C^2), 14.4 ($C^{2'}CH_3$). MS (ESI): m/z 310.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{18}H_{15}NNaO_2S^+$ 332.0721, found 332.0723.

*1-{5-[4-(Dimethylamino)benzoyl]-2-methyl-4-[4-(propan-2-yl)-phenyl]-1H-pyrrol-3-yl}ethanone (**7l**).* Following general procedure A, isoxazole **1l** (83.0 mg, 0.271 mmol) afforded the title compound (88.8 mg, 0.229 mmol, 84%) as a colorless solid. R_f = 0.19 (3:1 cyclohexane/ethyl acetate). Mp: 196.5−197.4 °C. IR (ATR): 1652, 1576, 1521, 1480, 1416, 1361, 1287, 1163, 921, 824, 774, 735. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 10.75 (br s, 1H, N*H*), 7.33−7.26 (m, 2H, $H^{2'''/6'''}$), 7.04−6.98 (m, 2H, $H^{2''/6''}$), 6.98−6.93 (m, 2H, $H^{3''/5''}$), 6.25−6.19 (m, 2H, $H^{3'''/5'''}$), 2.89 [s, 6H, $N(CH_3)_2$], 2.78 [septet, J = 6.9 Hz, 1H, $CH(CH_3)_2$], 2.60 (s, 3H, $C^{2'}CH_3$), 1.88 (s, 3H, H^2), 1.15 [d, J = 6.9 Hz, 6H, $CH(CH_3)_2$]. ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 197.9 (C^1), 186.6 ($C^{5'}CO$), 152.5 ($C^{4'''}$), 147.9 ($C^{4''}$), 139.2 ($C^{2'}$), 132.8 ($C^{1''}$), 132.0 ($C^{4'}$), 131.7 ($C^{2'''/6'''}$), 131.1 ($C^{2''/6''}$), 127.6 ($C^{5'}$), 125.9 ($C^{3''/5''}$), 124.9 ($C^{1'''}$), 123.8 ($C^{3'}$), 110.0 ($C^{3'''/5'''}$), 40.0 $[N(CH_3)_2]$, 33.9 $[CH(CH_3)_2]$, 31.0 (C^2), 24.0 $[CH(CH_3)_2]$, 14.3 ($C^{2'}CH_3$). MS (ESI): m/z 389.2 $[M + H]^+$. HRMS (ESI) calcd for $C_{25}H_{28}N_2NaO_2^+$ 411.2048, found 411.2048.

*1-{5-(4-Methoxybenzoyl)-2-methyl-4-[4-(trifluoromethyl)phenyl]-1H-pyrrol-3-yl}ethanone (**7m**).* Following general procedure A, isoxazole **1m** (60.0 mg, 0.188 mmol) afforded the title compound (69.6 mg, 0.173 mmol, 92%) as a colorless solid. R_f = 0.17 (3:1 cyclohexane/ethyl acetate). Mp: 154.6−155.7 °C. IR (ATR): 1602, 1483, 1422, 1324, 1256, 1166, 1124, 1067, 842, 775, 614. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 10.73 (br s, 1H, N*H*), 7.37−7.32 (m, 2H, $H^{3''/5''}$), 7.26−7.21 (m, 2H, $H^{2'''/6'''}$), 7.19−7.15 (m, 2H, $H^{2''/6''}$), 6.51−6.45 (m, 2H, $H^{3'''/5'''}$), 3.69 (s, 3H, OCH_3), 2.63 (s, 3H, $C^{2'}CH_3$), 1.91 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 196.6 (C^1), 186.8 ($C^{5'}CO$), 162.5 ($C^{4'''}$), 140.3 ($C^{2'}$), 139.1 ($C^{1''}$), 131.4 ($C^{2''/6''}$), 131.3 ($C^{4'}$), 131.1 ($C^{2'''/6'''}$), 129.8 ($C^{1'''}$), 129.5 (q, J = 32.6 Hz, $C^{4''}$), 127.5 ($C^{5'}$), 124.7 (q, J = 3.8 Hz, $C^{3''/5''}$), 124.1 (q, J = 272.2 Hz, CF_3), 124.0 ($C^{3'}$), 113.0 ($C^{3'''/5'''}$), 55.3 (OCH_3), 31.2 (C^2), 14.5 ($C^{2'}CH_3$). ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.9 (s, CF_3). MS (ESI): m/z 402.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{22}H_{18}F_3NNaO_3^+$ 424.1136, found 424.1127.

*1-[5-(2,2-Dimethylpropanoyl)-2-methyl-4-phenyl-1H-pyrrol-3-yl]-ethanone (**7n**).* Following general procedure A, isoxazole **1n** (96.9 mg, 0.481 mmol) afforded the title compound (40.1 mg, 0.142 mmol, 29%) as a colorless solid. A part of the starting isoxazole (62.7 mg, 0.312 mmol, 65%) was recovered unchanged. R_f = 0.36 (3:1 cyclohexane/ethyl acetate). Mp: 191.1−192.6 °C. IR (ATR): 3310, 2969, 1635, 1476, 1432, 1409, 1182, 935, 733, 700. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ 9.43 (br s, 1H, N*H*), 7.42−7.36 (m, 3H, $H^{3''/5''}$, $H^{4''}$), 7.33−7.29 (m, 2H, $H^{2''/6''}$), 2.55 (s, 3H, $C^{2'}CH_3$), 1.68 (s, 3H, H^2), 1.07 [s, 9H, $C(CH_3)_3$]. ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$): δ 198.4 ($C^{5'}CO$), 197.2 (C^1), 137.9 ($C^{2'}$), 136.7 ($C^{1''}$), 130.9 ($C^{2''/6''}$), 130.5 ($C^{4'}$), 128.2 ($C^{3''/5''}$), 128.1 ($C^{4''}$), 126.0 ($C^{5'}$), 124.2 ($C^{3'}$), 42.9 $[C(CH_3)_3]$, 30.8 (C^2), 27.6 $[C(CH_3)_3]$, 14.8 ($C^{2'}CH_3$). MS (ESI): m/z 284.2 $[M + H]^+$. HRMS (ESI) calcd for $C_{18}H_{22}NO_2^+$ 284.1651, found 284.1656.

*1-(5-Benzoyl-2-methyl-1H-pyrrol-3-yl)ethanone (**7o**).* Following general procedure A, isoxazole **1o** (80.0 μL, 91.1 mg, 0.627 mmol) afforded the title compound (121.6 mg, 0.535 mmol, 85%) as a colorless solid. R_f = 0.27 (3:1 cyclohexane/ethyl acetate). Mp: 210.9−211.6 °C. IR (ATR): 3247, 1669, 1608, 1548, 1506, 1290, 1142, 950, 728. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 10.79 (br s, 1H, N*H*), 7.94−7.88 (m, 2H, $H^{2''/6''}$), 7.65−7.58 (m, 1H, $H^{4''}$), 7.57−7.50 (m, 2H, $H^{3''/5''}$), 7.18 (d, J = 2.3 Hz, 1H, $H^{4'}$), 2.69 (s, 3H, $C^{2'}CH_3$), 2.44 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 194.7 (C^1), 185.0 ($C^{5'}CO$), 142.4 ($C^{2'}$), 137.9 ($C^{1''}$), 132.4 ($C^{4''}$), 129.1 ($C^{2''/6''}$), 128.7 ($C^{3''/5''}$), 128.6 ($C^{5'}$), 123.5 ($C^{3'}$), 121.7 ($C^{4'}$), 28.4 (C^2), 14.4 ($C^{2'}CH_3$). MS (ESI): m/z 228.1 $[M + H]^+$. HRMS (ESI) calcd for $C_{14}H_{14}NO_2^+$ 228.1025, found 228.1033.

*1-(5-Benzoyl-2-ethyl-4-phenyl-1H-pyrrol-3-yl)propan-1-one (**7p**).* Following general procedure B, isoxazole **1a** (90.0 mg, 0.407 mmol) and 3,5-heptanedione (**6b**, 110 μL, 104 mg, 0.814 mmol) afforded the title compound (126.3 mg, 0.381 mmol, 93%) as a colorless solid. R_f = 0.49 (3:1 cyclohexane/ethyl acetate). Mp: 144.6−145.5 °C. IR (ATR): 1597, 1574, 1463, 1416, 1257, 913, 735, 694. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 10.74 (br s, 1H, N*H*), 7.34−7.26 (m, 2H, $H^{2'''/6'''}$), 7.22−7.14 (m, 1H, $H^{4'''}$), 7.11−6.95 (m, 7H, $H^{2''/6''}$, $H^{3''/5''}$, $H^{4''}$, $H^{3'''/5'''}$), 3.02 (q, J = 7.4 Hz, 2H, $C^{2'}CH_2CH_3$), 2.06 (q, J = 7.2 Hz, 2H, H^2), 1.34 (t, J = 7.4 Hz, 3H, $C^{2'}CH_2CH_3$), 0.85 (t, J = 7.2 Hz, 3H, H^3). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 201.2 (C^1), 188.2 ($C^{5'}CO$), 145.5 ($C^{2'}$), 137.8 ($C^{1'''}$), 134.8 ($C^{1''}$), 133.3 ($C^{4'}$), 131.0 ($C^{4'''}$), 130.8 + 127.8 + 127.38 ($C^{2''/6''}$, $C^{3''/5''}$, $C^{3'''/5'''}$), 128.8 ($C^{2'''/6'''}$), 127.41 ($C^{4''}$), 127.0 ($C^{5'}$), 123.7 ($C^{3'}$), 35.8 (C^2), 21.2 ($C^{2'}CH_2CH_3$), 13.5 ($C^{2'}CH_2CH_3$), 8.6 (C^3). MS (ESI): m/z 332.2 $[M + H]^+$. HRMS (ESI) calcd for $C_{22}H_{21}NaNO_2^+$ 354.1470, found 354.1483.

*(3,5-Diphenyl-1H-pyrrole-2,4-diyl)bis(phenylmethanone) (**7q**).* Following general procedure B, isoxazole **1a** (80.0 mg, 0.362 mmol) and dibenzoylmethane (**6c**, 162.2 mg, 0.7233 mmol) afforded the title compound (113.5 mg, 0.2655 mmol, 73%) as a colorless solid. R_f = 0.47 (3:1 cyclohexane/ethyl acetate). Mp: 223.3−224.4 °C. IR (ATR): 3269, 1661, 1602, 1575, 1542, 1475, 1412, 1288, 738, 697. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ 9.87 (br s, 1H, N*H*), 7.67−7.62 (m, 2H, $H^{2'''/6'''}$), 7.55−7.51 (m, 2H, $H^{2''''/6''''}$), 7.44−7.39 (m, 2H, $H^{2'/6'}$), 7.36−7.27 (m, 4H, $H^{4''}$, $H^{3'''/5'''}$, $H^{4''''}$), 7.23−7.17 (m, 1H, $H^{4'}$), 7.16−7.11 (m, 2H, $H^{3''/5''}$), 7.04−6.98 (m, 2H, $H^{3'/5'}$), 6.96−6.92 (m, 2H, $H^{2''/6''}$), 6.90−6.81 (m, 3H, $H^{3''/5''}$, $H^{4''}$). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$): δ 194.3 (C^4CO), 187.7 (C^2CO), 138.1 ($C^{1'''}$), 137.9 (C^5), 137.4 ($C^{1'}$), 133.8 + 133.3 + 130.4 (C^3, $C^{1''}$, $C^{1''''}$), 132.9 ($C^{4'''}$), 131.5 ($C^{4'}$), 130.8 ($C^{2''/6''}$), 129.9 ($C^{2''/6'''}$), 129.3 ($C^{2'/6'}$), 129.1 ($C^{4''''}$), 129.0 ($C^{3'''/5'''}$), 128.1 ($C^{3''/5''}$), 128.0 ($C^{2'''/6'''}$ overlapping with C^2), 127.6 ($C^{3'/5'}$), 127.5 ($C^{3''/5''}$), 127.1 ($C^{4''}$), 123.4 (C^4). MS (ESI): m/z 428.2 $[M + H]^+$. HRMS (ESI) calcd for $C_{30}H_{21}NaNO_2^+$ 450.1470, found 450.1482. Analytical data in accordance with the literature.[22] Crystals suitable for X-ray crystallography could be obtained by recrystallization of **7q** from acetonitrile.

*(5-Methyl-3-phenyl-1H-pyrrole-2,4-diyl)bis(phenylmethanone) (**7r**)/1-(5-Benzoyl-2,4-diphenyl-1H-pyrrol-3-yl)ethanone (**7s**).* Following general procedure B, isoxazole **1a** (60.0 mg, 0.271 mmol) and benzoylacetone (**6d**, 87.9 mg, 0.542 mmol) afforded a nonseparable mixture (70.2 mg, 0.192 mmol, 71%) of the two isomers **7r** and **7s** (ratio of approximately 84:16 based on ^{1}H NMR integration) as a colorless oil. R_f = 0.39 (3:1 cyclohexane/ethyl acetate). IR (ATR): 3261, 1598, 1574, 1414, 1279, 907, 730, 695, 652. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$) for compound **7r**: δ 11.05 (br s, 1H, N*H*),

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7.54−7.51 (m, 2H, $H^{2'''/6'''}$), 7.37−7.33 (m, 2H, $H^{2'/6'}$), 7.25−7.22 (m, 1H, $H^{4'''}$), 7.18−7.14 (m, 1H, $H^{4'}$), 7.12−7.07 (m, 2H, $H^{3'''/5'''}$), 6.99−6.94 (m, $H^{3'/5'}$), 6.81−6.75 (m, 3H, $H^{2''/6''}$, $H^{4''}$), 6.74−6.70 (m, 2H, $H^{3''/5''}$), 2.53 (s, 3H, CH_3); for compound **7s** (signals partially superimposed): δ 10.71 (br s, 1H, N*H*), 7.67−7.65 (m, 2H, $H^{2''/6''}$), 7.45−7.42 (m, 3H, $H^{3''/5''}$, $H^{4''}$), 7.39−7.37 (m, 2H, $H^{2'''/6'''}$), 7.22−7.18 (m, 1H, $H^{4'''}$), 7.12−7.04 (m, 5H, $H^{2'''/6'''}$, $H^{3'''/5'''}$, $H^{4'''}$), 7.04−7.00 (m, 2H, $H^{3'''/5'''}$), 1.96 (s, 3H, H^2). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) for compound **7r**: δ 194.1 (C^4CO), 188.0 (C^2CO), 139.6 (C^5), 138.8 ($C^{1'''}$), 137.5 ($C^{1'}$), 134.2 (C^3), 133.7 ($C^{1''}$), 132.0 ($C^{4'''}$), 131.3 ($C^{4'}$), 131.0 ($C^{2''/6''}$), 129.6 ($C^{2'''/6'''}$), 129.27 ($C^{2'/6'}$), 127.74 ($C^{3'''/5'''}$), 127.42 ($C^{3'/5'}$), 127.2 ($C^{3''/5''}$), 126.6 (C^2, $C^{4''}$), 123.2 (C^4), 13.2 (CH_3); for compound **7s**: 198.6 (C^1), 188.1 ($C^{5'}CO$), 139.1 ($C^{2'}$), 137.4 ($C^{1'''}$), 133.8 ($C^{1'''}$), 133.3 ($C^{4'}$), 131.4 ($C^{4'''}$), 130.89 ($C^{1''}$), 130.86 ($C^{2''/6''}$), 129.31 ($C^{4''}$), 129.10 + 129.09 ($C^{2''/6''}$, $C^{2'''/6'''}$), 128.7 ($C^{3''/5''}$), 128.2 ($C^{5'}$), 127.76 ($C^{3'''/5'''}$), 127.51 ($C^{3'''/5'''}$), 127.45 ($C^{4'''}$), 125.4 ($C^{3'}$), 31.7 (C^2). MS (ESI): *m*/*z* 366.2 $[M + H]^+$. HRMS (ESI) calcd for $C_{25}H_{19}NaNO_2^+$ 388.1313, found 388.1302.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00511.

Reaction monitoring, NMR spectra, crystallographic data for compounds **7a** and **7q**, and ESI-MS experiments (PDF)

Crystallographic data for **7a** (CIF)

Crystallographic data for **7q** (CIF)

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Notes

The authors declare no competing financial interest.

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