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REGIOSELECTIVE SYNTHESIS OF 2,4-(DIOXOBUTYL)DIHYDRO-QUINOLINES AND –PYRIDINES BY CHLOROFORMIATE-MEDIATED REACTION OF 1,3-BIS(SILYL ENOL ETHERS) WITH QUINOLINES AND PYRIDINES

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Abstract – 2,4-(Dioxobutyl)dihydroquinolines and –pyridines were prepared by chloroformiate-mediated reaction of 1,3-bis(silyl enol ethers) with quinolines and pyridines.

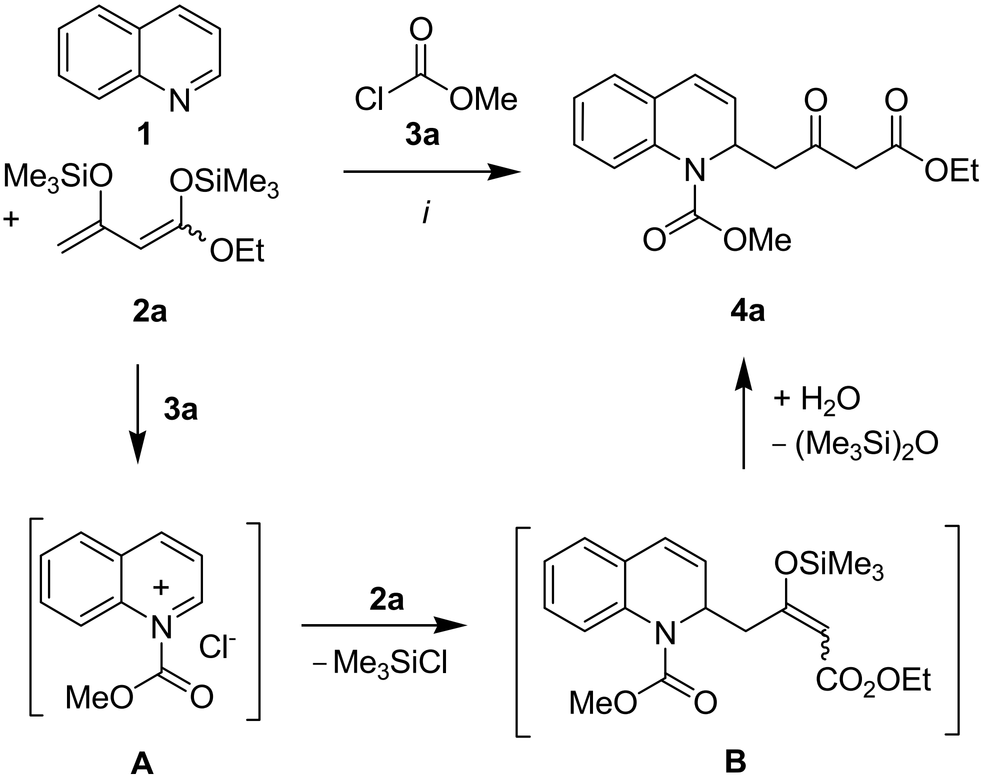
INTRODUCTION

Quinoline, isoquinoline, and pyridine and their derivatives are of considerable pharmacological relevance and are present in various antibiotics[1, 2, 3] and natural products.[4, 5] Quinolinium- and isoquinolinium salts, generated by alkylation or acylation of quinoline and isoquinoline, represent important synthetic building blocks for the synthesis of such compounds.[6] Quinolines have been functionalized by the Reissert reaction. The classic variant relies on the reaction of KCN in the presence of acylating agents. In a more recent variant TMSCN in the presence of a fluoride source is employed.[3, 7, 8] The addition of Grignard reagents to quinoline was reported to give 1,2-dihydroquinolines.[9] The ethyl chloroformiate mediated reaction of a quinoline with (trimethylsilylethinyl)magnesium chloride was used for the synthesis of endiyne-antibiotics.[9] Addition reactions of zink-,[10] tin-[11,12] and titanium-organometallic reagents[13] to quinoline derivatives have been reported. Palladino *et al.* reported the benzoyl chloride mediated addition of ethyl acetoacetate to quinoline to give 2,3-dihydroquinolines.[14] The reaction of 4-silyloxyquinolinium triflates with enamines afforded 2-substituted 4-silyloxy-1,2-dihydroquinolines.[15] The reaction of quinolinium salts with allylsilanes in the presence of AgOTf[16] and ethyl trimethylsilylacetate[17, 18] afforded regioisomeric mixtures of 2- and 4-substituted dihydroquinolines. Reddy *et al.* reported the synthesis of benzazepines by reaction of quinolinium- and isoquinolinium salts with diazoesters.[19] Two-step cyclocondensations of 1,1-bis(trimethylsilyloxy)ketene acetals with quinoline and isoquinoline have been reported by Rudler[20] and ourselves.[21] Tropane derivatives were prepared by cyclization of 1,3-bis(silyl enol ethers)[22] with bis(iminium) salts of 2,5-dimethoxypyrrolidines.[23] Recently, the cyclocondensation of 1,3-bis(silyl enol ethers) with isoquinolines,[24] quinoxalines[25] and quinazolines was reported.[26] Herein, we report a facile synthesis of 2,4-(dioxobutyl)dihydroquinolines and –pyridines by what are, to the best of our knowledge, the first condensation reactions of 1,3-bis(silyl enol ethers) with quinolines and pyridines.

RESULTS AND DISCUSSION

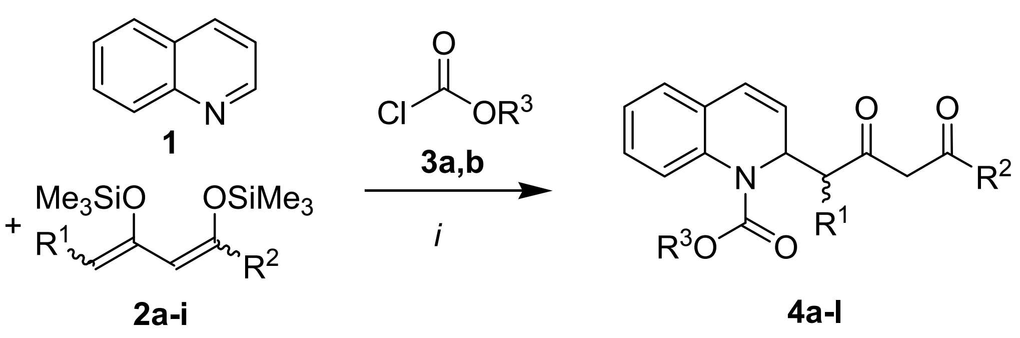
1,3-Bis(silyl enol ethers) **2** are available from the corresponding 1,3-dicarbonyl compounds in one or two steps.[27] The reaction of quinoline (**1**) with 1,3-bis(silyl enol ether) **2a**, in the presence of methyl chlorformate (**3a**), afforded 2,3-dihydroquinoline **4a** (Scheme 1). The best yields were obtained when an excess of **2a** and of **3a** was employed. The reactions were carried out at 0 °C. The yields dropped when the reactions were carried out at −78 °C or at 20 °C. Notably, the yield dramatically decreased when benzyl rather than methyl chloroformiate was used (vide infra). A complex mixture was formed when 1.2 equiv.of benzenesulfonyl chloride or 4-nitrobenzoyl chloride were employed. The formation of **4a** can be explained by formation of quinolinium salt **A**, regioselective attack of the terminal carbon atom of **2a** onto carbon atom C-2 of the quinolinium salt to give intermediate **B**, and subsequent hydrolysis.

1,3-Bis(silyl enol ethers) **2a-e** were prepared from methyl, ethyl, isopropyl, methoxyethyl and isobutyl acetoacetate, respectively (Scheme 2, Table 1).[27] The reaction of **2a-d** with quinoline, in the presence of methyl chloroformiate (**3a**), afforded 1,2-dihydroquinolines **4a-d** in moderate to good yields. The reaction of **2a** and **2b** with **1**, in the presence of benzyl chloroformiate (**3b**) rather than methyl chloroformiate (**3a**), afforded 2,3-dihydroquinolines **4e** and **4f**, however, in only low yield. The benzyl chloroformiate mediated reaction of quinoline with **2d** and **2e** afforded 1,2-dihydroquinolines **4g** and **4h** in moderate yields. The reaction of 1,3-bis(silyl enol ethers) **2f** and **2g**, prepared from acetylacetone and benzoylacetone, afforded 2,3-dihydroquinolines **4i** and **4j** in good yields, respectively.



Scheme 1. Mechanism of the formation of **4a**, *i*: CH_2Cl_2, 0 → 20 °C, 16 h

The benzyl chloroformiate mediated reaction of 1,3-bis(silyl enol ethers) **2h** and **2i**, prepared from ethyl 3-oxohexanoate and ethyl 4-ethoxyacetoacetate, afforded 1,2-dihydroquinolines **4k** and **4l**, respectively. Reactions of substituted quinoline derivatives have not been studied. All reactions proceeded with excellent regioselectivity. The isolated products were regioisomerically pure (>98:2). The formation of the other regioisomers, formed by attack of the diene to carbon C-4 of the quinoline, was not observed.



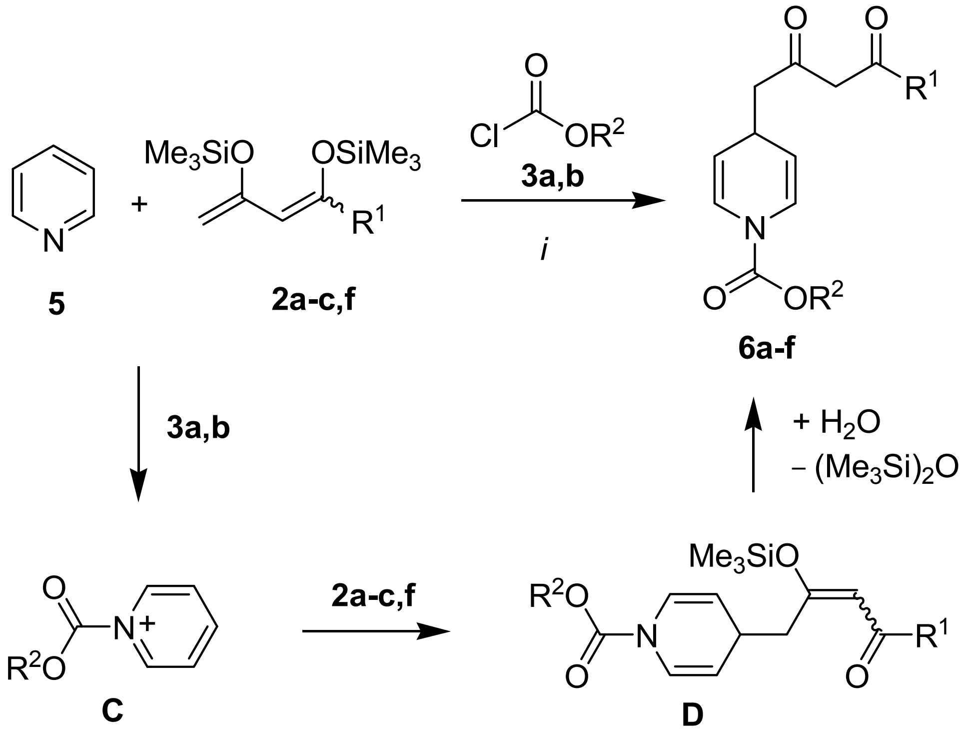
Scheme 2. Synthesis of dihydroquinolines **4a-l**; *i*: CH_2Cl_2, 0 → 20 °C, 16 h

Table 1. Products and yields

2	*3*	*4*	*R*[1]	*R*[2]	*R*[3]	%[a]
a	**a**	**a**	H	OEt	Me	50
b	**a**	**b**	H	OMe	Me	54
c	**a**	**c**	H	O*i*Pr	Me	90
d	**a**	**d**	H	$O(CH_2)_2OMe$	Me	36
a	**b**	**e**	H	OEt	Bn	14
b	**b**	**f**	H	OMe	Bn	24
d	**b**	**g**	H	$O(CH_2)_2OMe$	Bn	39
e	**b**	**h**	H	O*i*Bu	Bn	47
f	**a**	**i**	H	Me	Me	83
g	**a**	**j**	H	Ph	Me	68
h	**b**	**k**	Et	OEt	Bn	28
i	**b**	**l**	OEt	OEt	Bn	46

[a] Yields of isolated products

The methyl chloroformiate mediated reaction of pyridine (**5**) with 1,3-bis(silyl enol ether) **2a**, carried out following the procedure as developed for the analogous reactions of quinoline, afforded the unstable 1,4-dihydropyridine **6a** in low yield (Scheme 3, Table 2). The formation of **6a** can be explained by formation of pyridinium salt **C**, regioselective attack of the terminal carbon atom of **2a** onto carbon atom C-4 of the pyridinium salt to give intermediate **D**, and subsequent hydrolysis. It is noteworthy that the same regioselectivity was previously observed for the ethyl chloroformiate mediated reaction of pyridine with simple silyl enol ethers.[28] The reaction of **5** with 1,3-bis(silyl enol ethers) **2b** and **2c**, in the presence of **3a**, afforded 1,4-dihydropyridines **6b** and **6c**, again, in low yields. In contrast to the corresponding reactions of quinoline, where the use of benzyl rather than methyl chloroformiate resulted in a decrease in yield, a considerably higher yield was obtained in the reaction of 1,3-bis(silyl enol ethers) **2a** and **2b** with pyridine when benzyl chloroformiate was employed (products **6d** and **6e**). The reaction of pyridine with 1,3-bis(silyl enol ether) **2f** afforded 1,4-dihydropyridine **6f**. The best yield was obtained when methyl chloroformiate was used as the activating agent. The employment of 4-picoline or 2,6-lutidine proved to be unsuccessful. All reactions proceeded with excellent regioselectivity. The isolated products were regioisomerically pure (>98:2). The formation of the other regioisomers, formed by attack of the diene to carbon C-2 of the pyridine, was not observed.



Scheme 3. Synthesis of 1,4-dihydropyridines **6a-f**, *i*: CH_2Cl_2, 0 → 20 °C, 16 h

Table 2. Products and yields

6	*R¹*	*R²*	*%ᵃ*
a	OEt	Me	22
b	OMe	Me	21
c	$O(CH_2)_2OMe$	Me	20
d	OEt	Bn	66
e	OMe	Bn	63
f	Me	Me	35

[a] Yields of isolated products

The different regioselectivities observed for the reactions of 1,3-bis(silyl enol ethers) **2** with quinoline and pyridine might be explained by the assumption that the attack of the diene onto carbon atom C-4 is more sterically hinderd than the attack to C-2. The fused benzene moiety might have a stronger steric influence than the carbamate moiety. In the case of pyridine, there is no steric hindrance associated with the attack of the diene to carbon atom C-4. On the other hand, the attack of the diene to carbon C-2 is hindered by the steric influence of the carbamate group. In addition, electronic reasons might play a role.

It is worth to be noted that, for pyridine, benzyl chloroformiate gave much better results than methyl chloroformiate. The opposite is true for quinoline. This might be explained by solubility reasons. In addition, the attack of the diene to carbon atom C-2 of the quinoline is more sterically hindered by the benzyl- than by the methyl-substituted carbamate moiety. This steric hindrance plays not a role in case of pyridine as the attack of the diene occurs at carbon C-4 of the pyridine moiety.

In conclusion, we reported the synthesis of 2,4-(dioxobutyl)dihydroquinolines and –pyridines by chloroformiate-mediated reaction of 1,3-bis(silyl enol ethers) with quinolines and pyridines.

EXPERIMENTAL

General. All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^{1}H and ^{13}C NMR, the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (70 eV), chemical ionization (CI, H_2O) or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60-200 mesh) was used. Melting points are uncorrected.

General procedure for the reaction of 1,3-bis(silyl enol ethers) with quinoline and pyridine. To a CH_2Cl_2 solution of quinoline or pyridine and of the 1,3-bis(silyl enol ether) was added the cloroformate at 0 °C. The solution was allowed to warm to 20 °C during 16 h and an aqueous solution of NH_4Cl (20 mL, 1 M) was added. The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/EtOAc = 5:1). Due to the hindered rotation of the carbon-nitrogen bond of the carbamate group, a doubling of some signals was observed in ^{1}H and ^{13}C NMR.

Ethyl 4-(1-*N*-methoxycarboyl-2-dihydroquinolyl)-3-oxobutanoate (4a). Starting with **1** (0.194 g, 1.5 mmol), **3a** (0.161 g, 1.7 mmol) and **2a** (0.822 g, 3.0 mmol), **4a** was isolated as a yellow oil (0.237 g, 50%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.22 (t, ^3J = 7.0 Hz, 3 H, CH_3), 2.70 (ddd, ^3J = 18.0 Hz, ^3J = 8.0 Hz, ^3J = 6.0 Hz, 2 H, CH_2), 3.41 (d, ^3J = 8.0 Hz, 1 H, CH CH_2), 3.70 (s, 3 H, CH_3), 4.16 (q, ^3J = 7.0 Hz, 2 H, CH_2), 5.49 (ddd, ^3J = 6.0 Hz, 1 H, CH), 6.14 (dd, $^3J_{cis}$ = 10.0 Hz, ^3J = 6.0 Hz, 1 H, CH), 6.49 (d, $^3J_{cis}$ = 10.0 Hz, 1 H, CH), 7.08-7.10 (m, 2 H, CH), 7.21 -7.25 (m, 1 H, CH), 7.55 (d, ^3J = 8.0 Hz, 1 H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 46.6 (CH_2), 48.8 (CH), 49.5 (CH_2), 53.2 (CH_3), 61.4 (CH_2), 124.6, 124.6, 125.5, 126.4, 126.8, 127.8 (CH), 128.4, 133.9, 154.5, 166.8, 200.0 (C). MS (EI, 70 eV): *m/z* = 316 (M^+, 84), 214 (16), 183 (57), 169 (51), 116 (100). Anal. Calcd for $C_{17}H_{19}NO_5$: C, 64.34; H, 6.03; N, 4.41. Found: C, 64.07; H, 5.64; N, 3.93.

Methyl 4-(1-*N*-methoxycarboyl-2-dihydroquinolyl)-3-oxobutanoate (4b). Starting with **1** (2.0 mmol, 1.0 equiv.), CH_2Cl_2 (20 mL) **2b** (4.0 mmol, 2.0 equiv.) and **3a** (0.23 g, 2.4 mmol, 1.2 equiv.), **4b** was isolated by chromatography (silica gel, hexane/EtOAc = 7:1) as a yellow oil (0.33 g, 54%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.62 - 2.80 (m, 2 H, CH_2), 3.37 - 3.50 (m, 2 H, CH_2, keto), 3.71, 3.73 (2 x s, 3 H, CH_3, keto, enol) 3.78, 3.80 (2 x s, 3 H, CH_3, keto, enol), 4.89 (s, 1 H, CH, enol), 5.49 (dt, ^3J = 6.0 Hz, 1 H, CH), 6.14 (dd, ^3J = 6.0 Hz, $^3J_{cis}$ = 9.0 Hz, 1 H, CH), 6.49 (d, $^3J_{cis}$ = 9.0 Hz, 1 H, CH), 7.08 - 7.11 (m, 2 H, CH), 7.21 - 7.24 (m, 1 H, CH), 7.55 (br d, ^3J = 8.0 Hz, 1 H, CH), 11.97 (s, 1 H, OH, enol). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 46.4 (CH_2), 48.7 (CH_3), 49.1 (CH_2), 52.3 (CH_3), 53.1 (CH), 124.5, 125.5, 125.6, 126.3 (CH), 126.7 (C), 127.7, 128.2 (CH), 133.8, 154.4, 167.1, 199.8 (C). UV-Vis (λ, log ε): 231.49 (4.6). IR (KBr): $\tilde{\nu}$ = 3033 (w), 3003 (w), 2956 (m), 1748 (s), 1714 (s), 1658 (m), 1604 (w), 1572 (w), 1528 (w), 1490 (s), 1440 (s). MS (EI, 70 eV): *m/z* (%) = 303 (M^+, 1), 244 (6), 188 (100), 144 (48), 129 (12). Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.30; H, 6.08; N, 4.79.

Isopropyl 4-(1-*N*-methoxycarboyl-2-dihydroquinolyl)-3-oxobutanoate (4c). Starting with **1** (0.129 g, 1.0 mmol), **3a** (0.104 g, 1.1 mmol) and **2c**, **4c** was isolated as a yellow oil (0.283 g, 90%, keto/enol = 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.22 (d, ^3J = 7.0 Hz, 6H, CH_3), 2.62, 2.67, (d, ^3J = 6.0 Hz, 1H, CH_2, keto, enol), 2.73, 2.79 (d, ^3J = 8.0 Hz, 1H, CH_2, keto, enol), 3.30, 3.35 (s, 1H, CH_2, keto, enol), 3.38, 3.44 (s, 1H, CH_2, keto, enol), 3.78 (s, 3H, CH_3), 5.02 (sep., ^3J = 7.0 Hz, 1H, CH), 5.49 (ddd, ^3J = 6.0 Hz, ^3J = 6.0 Hz, ^3J = 8.0 Hz, 1H, CH), 6.15 (dd, ^3J = 10.0 Hz, ^3J = 6.0 Hz, 1H, CH), 6.48 (d, ^3J = 10.0 Hz, 1H, CH), 7.07 – 7.10 (m, 2H, CH), 7.20 – 7.26 (m, 1H, CH), 7.54 – 7. 56 (m, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.0 (CH_3), 46.9 (CH_2), 49.2 (CH), 50.2 (CH_2), 53.6, 69.5, 125.0, 125.9, 126.1, 126.8 (CH), 127.2 (C), 128.2, 128.8 (CH), 134.0, 154.6, 166.3, 200.1 (C). IR (KBr): $\tilde{\nu}$ = 3443 (w), 3037 (w), 2983 (m), 2958 (m), 2856 (w), 1710 (s), 1645 (m), 1611 (w), 1577 (w), 1490 (s), 1442 (s) cm^{-1}. UV-Vis (MeCN): λ_{max} (lg ε) = 234.92 (4.43) nm. MS (EI, 70 eV): *m/z* = 331 (M^+, 1), 272 (8), 188 (100), 144 (69), 129 (14). Anal. Calcd for $C_{18}H_{21}NO_5$: C, 65.24; H, 6.39; N, 4.23. Found: C, 64.87; H, 6.74; N, 3.99.

Methoxyethyl 4-(1-*N*-methoxycarboyl-2-dihydroquinolyl)-3-oxobutanoate (4d). Starting with **1** (0.39 g, 3.0 mmol, 1.0 equiv.), **2c** (1.83 g 6.0 mmol, 2.0 equiv.), **3a** (0.34 g, 3.6 mmol, 1.2 equiv.) and CH_2Cl_2 (20 mL), **4d** was isolated by chromatography (silica gel, hexane/EtOAc = 3:1 → 2:1) as a yellow oil (0.37 g, 36%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.63 – 2.81 (m, 2 H, CH_2), 3.26 – 3.62 (m, 7 H, CH_2, CH_2, CH_3), 3.78, 3.79 (2 x s, 3 H, CH_3), 4.25 – 4.29 (m, 2 H, CH_2), 4.95 (s, 1 H, CH, enol), 5.49 (dt, ^3J =

7.0 Hz, 1 H, CH), 6.14 (dd, ^3J = 6.0 Hz, $^3J_{cis}$ = 9.0 Hz, 1 H, CH), 6.49 (d, $^3J_{cis}$ = 9.0 Hz, 1 H, CH), 7.07 – 7.10 (m, 2 H, CH), 7.21 – 7.26 (m, 1 H, CH), 7.55 (m, 1 H, CH), 11.95 (s, 1 H, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 46.5 (CH_2), 48.8 (CH_3), 49.3 (CH_2), 50.2 (CH_3), 53.2 (CH), 64.2 (CH_2), 70.1 (CH_2), 124.6, 125.7, 126.3, 126.4 (CH), 126.9 (C), 127.8, 128.3 (CH), 133.9, 154.4, 166.8, 199.8 (C). UV-Vis (λ, log ε): 231.40 (4.5). IR (KBr): $\tilde{\nu}$ = 2955 (w), 2931 (w), 2894 (w), 1744 (s), 1656 (w), 1489 (m), 1441 (s). MS (EI, 70 eV): *m/z* (%) = 347 (M^+, 1), 188 (100), 144 (51), 129 (22), 60 (16). Anal. Calcd for $C_{18}H_{21}NO_6$: C, 62.24; H, 6.09; N, 4.03. Found: C, 61.98; H, 6.14; N 4.19.

Ethyl 4-(1-*N*-benzyloxycarboyl-2-dihydroquinolyl)-3-oxobutanoate (4e). Starting with **1** (0.26 g, 2.0 mmol, 1.0 equiv.), **2a** (1.098 g, 4.0 mmol, 2.0 equiv.), **3b** (0.41 g, 2.4 mmol, 1.2 equiv.), and CH_2Cl_2 (20 mL), **4e** was isolated by chromatography (silica gel, hexane/EtOAc = 7:1) as a yellow oil (0.109 g, 14%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.20 - 1.31 (t, ^3J = 7.0 Hz, 3 H, CH_3), 2.68 - 2.75 (m, 2 H, CH_2), 3.03 - 3.39 (m, 2 H, CH_2, keto), 4.11 - 4.18 (q, ^3J = 7.0 Hz, 2 H, CH_2), 4.86 (s, 1 H, CH, enol), 5.17 - 5.32 (m, 2 H, CH_2), 5.51 (dt, ^3J = 6.0 Hz, 1 H, CH), 6.13 (dd, ^3J = 6.0 Hz, $^3J_{cis}$ = 9.0 Hz, 1 H, CH), 7.08 - 7.10 (m, 2 H, CH_2), 7.20 - 7.23 (m, 1 H, CH), 7.31 - 7.38 (m, 5 H, CH), 7.56 (m, 1 H, CH), 12.04 (s, 1 H, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 46.4 (CH_2), 48.8 (CH_3), 49.4 (CH_2), 50.3 (CH), 61.3 (CH_2), 67.9 (CH_2), 124.6, 125.5, 126.4, 126.7 (CH), 127.7 (C), 127.9, 128.0, 128.0, 128.1, 128.3, 128.5 (CH), 133.8, 153.7, 166.7, 199.9 (C). IR (KBr): $\tilde{\nu}$ = 2983 (w), 1743 (s), 1652 (m), 1606 (w), 1491 (m), 1455 (m). UV-Vis (λ, log ε): 203.87 (4.6), 232.11 (4.5). MS (EI, 70 eV) *m/z* (%) = 393 (M^+, 1), 264 (14), 220 (18), 129 (6), 91 (100). Anal. Calcd for $C_{23}H_{23}NO_5$: C, 70.22; H, 5.89; N 3.56. Found: C, 70.10; H, 6.16; N, 3.51.

Methyl 4-(1-*N*-benzyloxycarboyl-2-dihydroquinolyl)-3-oxobutanoate (4f). Starting with **1** (0.26 g, 2.0 mmol, 1.0 equiv.), **2b** (1.04 g, 4.0 mmol, 2.0 equiv.), **3b** (0.82 g, 50% solution in toluene, 2.4 mmol, 1.2 equiv.), and 20 mL of CH_2Cl_2, **4f** was isolated by chromatography (silica gel, hexane/EtOAc = 7:1) as a yellow oil (0.18 g, 24%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.68 - 2.74 (m, 2 H, CH_2), 3.33 - 3.41 (m, 2 H, CH_2, keto), 3.69, 3.72 (2 x s, 3 H, CH_3, keto, enol), 4.88 (s, 1 H, CH, enol), 5.17 - 5.32 (m, 2 H, CH_2), 5.54 (dt, ^3J = 6.0 Hz, 1 H, CH), 6.13 (dd, ^3J = 6.0 Hz, $^3J_{cis}$ = 9.0 Hz, 1 H, CH), 6.49 (d, $^3J_{cis}$ = 9.0 Hz, 1 H, CH) 7.08 - 7.10 (m, 2 H, CH), 7.19 - 7.24 (m, 1 H, CH), 7.32 - 7.37 (m, 5 H, CH), 7.55 (m, 1 H, CH), 11.97 (s, 1 H, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 46.5 (CH_2), 48.9 (CH_3), 49.2 (CH_2), 52.4 (CH), 68.0 (CH_2), 124.7, 125.6, 125.8, 126.4 (CH), 126.8 (C), 127.8, 127.9, 128.1, 128.1, 128.2, 128.6 (CH), 133.9, 153.9, 167.2, 199.8 (C). IR (KBr): $\tilde{\nu}$ = 1747 (m), 1711 (s), 1657 (w), 1634 (w), 1491 (m), 1452 (m), 1441 (m). UV-Vis (λ, log ε): 206.69 (4.2), 235.66 (4.5). MS (EI, 70 eV): *m/z* (%) = 379 (M^+, 3), 264 (59), 220 (67), 142 (36), 91 (100). Anal. Calcd for $C_{22}H_{21}NO_5$: C, 69.65; H, 5.58; N, 3.69. Found: C, 69.31; H, 5.81; N, 3.64.

Methoxyethyl 4-(1-*N*-benzyloxycarboyl-2-dihydroquinolyl)-3-oxobutanoate (4g). Starting with **1** (0.26 g, 2.0 mmol, 1.0 equiv.), **2d** (1.22 g, 4.0 mmol, 2.0 equiv.), **3b** (0.41 g, 2.4 mmol, 1.2 equiv.), and 20 mL of CH_2Cl_2, **4g** was isolated by chromatography (silica gel, hexane/EtOAc = 4:1) as a yellow oil (0.327 g, 39%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 2.69 - 2.75 (m, 2 H, CH_2), 3.18 - 3.62 (m, 7 H, CH_2, CH_2, CH_3), 4.23 - 4.32 (m, 2 H, CH_2), 4.94 (s, 1 H, CH, enol), 5.16 - 5.32 (m, 2 H, CH_2, keto, enol), 5.51 (dt, ^3J = 6.0 Hz, 1 H, CH), 6.14 (dd, ^3J = 6.0 Hz, $^3J_{cis}$ = 9.0 Hz, 1 H, CH), 6.48 (d, ^3J = 6.0 Hz, $^3J_{cis}$ = 9.0 Hz, 1 H, CH), 7.08 - 7.10 (m, 2 H, CH), 7.20 - 7.22 (m, 1 H, CH), 7.31 - 7.36 (m, 5 H, CH), 7.55 (m, 1 H, CH), 11.91 (s, 1 H, OH). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 45.5 (CH_2), 47.9 (CH_3), 48.3 (CH_2), 57.9 (CH_3), 63.2 (CH), 66.3 (CH_2), 66.8 (CH_2), 69.1 (CH_2), 123.6, 124.5, 125.4, 125.4 (CH), 126.6 (C), 126.9, 127.0, 127.2, 127.2, 127.6 (CH), 135.5, 152.5, 166.7, 199.8 (C). UV-Vis (λ, log ε): 232.18 (4.5). IR (KBr) $\tilde{\nu}$ = 3064 (w), 3038 (w), 2981 (m), 2956 (w), 2932 (w), 2892 (m), 1654 (m), 1606 (m) 1572 (w), 1491 (s), 1454 (s). MS (EI, 70 eV) : *m/z* (%) = 425 (M^+, 1), 264 (10), 220 (17), 129 (10), 91 (100), 45 (10). Anal. Calcd for $C_{24}H_{25}NO_6$: C, 68.07; H, 5.95; N, 3.31. Found: C, 67.86; H, 6.00; N, 3.38.

Isobutoxy 4-(1-*N*-benzyloxycarboyl-2-dihydroquinolyl)-3-oxobutanoate (4h). Starting with **1** (0.26 g, 2.0 mmol, 1.0 equiv.), **2e** (1.21 g, 4.0 mmol, 2.0 equiv.), **3b** (0.41 g, 2.4 mmol, 1.2 equiv.), and 20 mL of CH_2Cl_2, **4h** was isolated by chromatography (silica gel, hexane/EtOAc = 7:1) as a yellow oil (0.399 g, 47%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.91 (d, ^3J = 7.0 Hz, 6 H, CH_3), 1.87 (tqq, ^3J = 8.0 Hz, 1 H, CH), 2.61 - 2.80 (m, 2 H, CH_2), 3.32 - 3.45 (m, 2 H, CH_2, keto), 3.86 (d, ^3J = 7.0 Hz, 2 H, CH_2), 4.89 (s, 1 H, CH, enol), 5.16 - 5.31 (m, 2 H, CH_2), 5.53 (dt, ^3J = 7.0 Hz, 1 H, CH), 6.14 (dd, ^3J = 6.0 Hz, $^3J_{cis}$ = 9.0 Hz, 1 H, CH), 6.49 (d, $^3J_{cis}$ = 9.0 Hz, 1 H, CH), 7.07 - 7.09 (m, 2 H, CH), 7.18 - 7.24 (m, 1 H, CH), 7.31 - 7.32 (m, 5 H, CH), 7.55 (m, 1 H, CH), 12.03 (s, 1 H, OH). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 46.7 (CH_2), 49.0 (CH_3), 49.5 (CH_2), 50.5 (CH_3), 68.0 (CH), 124.5, 125.6, 125.8, 126.4 (CH), 126.5 (C), 127.7, 127.9, 128.1, 128.1, 128.2, 128.4 (CH), 133.8, 153.7, 166.7, 199.9 (C). UV-Vis (λ, log ε): 325.69 (4.5). IR (KBr): $\tilde{\nu}$ = 2963 (m), 1741 (s), 1652 (w), 1491 (m), 1457 (w). MS (EI, 70 eV): *m/z* (%) = 423 (M^+, 1), 264 (16), 220 (28), 212 (10), 91 (100). Anal. Calcd for $C_{25}H_{27}NO_5$: C, 71.24; H, 6.46; N, 3.32. Found: C, 71.09; H, 7.07; N, 3.46.

1-(1-*N*-Methoxycarboyl-2-dihydroquinolyl)-2,4-dioxopentane (4i). Starting with **1** (0.194 g, 1.5 mmol), **3a** (0.161 g, 1.7 mmol) and **2f** (0.732 g, 3.0 mmol), **4i** was isolated as a yellow oil (0.356 g, 83%, keto/enol = 2:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.95 (s, 3 H, CH_3), 2.28, 2.31 (d, ^3J = 7.0 Hz, 2 H, CH$_2$), 3.70 (s, 3 H, CH$_3$), 5.32 (s, 1 H, CH), 5.34 (dt, ^3J = 7.0 Hz, 1 H, CH), 6.00 (dd, ^3J = 7.0 Hz, $^3J_{\mathrm{cis}}$ = 10.0 Hz, 1 H, CH), 6.44 (d, $^3J_{\mathrm{cis}}$ = 10.0 Hz, 1 H, CH), 7.01 – 7.03 (m, 2 H, CH), 7.15 – 7.19 (m, 1 H, CH), 7.45 – 7.53 (m, 1 H, CH), 15.25 (br, 1 H, OH). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 25.1 (CH$_3$), 41.5 (CH$_2$), 50.1 (CH), 53.1 (CH$_3$), 57.8 (CH$_2$, keto), 100.9 (CH, enol), 124.5, 124.6, 125.6, 126.4 (CH), 126.9 (C), 127.8, 128.2 (CH), 134.0 (C), 154.5, 189.2, 191.9 (CO). IR (KBr): $\tilde{\nu}$ = 3409 (w), 3068 (w), 3037 (w), 2975 (m), 2931 (w), 2862 (w), 1711 (s), 1623 (s), 1532 (m), 1490 (s), 1441 (s) cm^{-1}. UV-Vis (MeCN): $\lambda_{\max}$ (lg ε) = 230.71 (4.33) nm. MS (EI, 70 eV): *m/z* = 287 (M$^+$, 2), 228 (4), 188 (100), 144 (69), 129 (20). Anal. Calcd for $C_{16}H_{17}NO_5$: C, 66.89; H, 5.96; N, 4.88. Found: C, 67.09; H, 6.23; N, 5.25.

4-(1-*N*-Methoxycarboyl-2-dihydroquinolyl)-1,3-dioxo-1-phenylbutane (4j): Starting with **1** (0.194 g, 1.5 mmol), **3a** (0.161 g, 1.7 mmol) and **2g** (0.918 g, 3.0 mmol), **4j** was isolated as a yellow oil (0.354 g, 68%, keto/enol > 98:2). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 3.02 (dt, ^3J = 7.0 Hz, 2 H, CH$_2$), 4.25 (s, 1 H, CH$_3$), 6.03 (dt, ^3J = 7.0 Hz, 1 H, CH), 6.58 (s, 1 H, CH), 6.61 (dd, ^3J = 7.0 Hz, $^3J_{\mathrm{cis}}$ = 10.0 Hz, 1 H, CH), 7.03 (d, $^3J_{\mathrm{cis}}$ = 10.0 Hz, 1 H, CH), 7.60 – 7.62 (m, 2 H, CH), 7.72 – 7.77 (m, 1 H, CH), 7.90 – 8.14 (m, 4 H, CH), 8.33 – 8 35 (m, 2 H, CH), 16.53 (br. s, 1 H, OH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 42.26 (CH$_2$), 50.15 (CH), 53.07 (CH$_3$), 97.03 (CH), 121.34, 124.50 (CH), 125.07 (C), 125.64, 126.40, 127.02, 127.79, 128.53, 128.59, 132.42 (CH), 134.00, 134.74, 154.48, 183.88, 191.74 (C). IR (KBr): $\tilde{\nu}$ = 3067 (w), 2955 (s), 2926 (s), 2857 (m), 1728 (s), 1668 (m), 1603 (s), 1573 (s), 1489 (s), 1443 (s) cm^{-1}. UV-Vis (MeCN): $\lambda_{\max}$ (lg ε) = 205.84 (4.06), 232.02 (4.07) nm. MS (EI, 70 eV): *m/z* = 349 (M$^+$,2), 290 (7), 210 (6), 188 (100), 144 (77). HRMS (EI, 70 eV): Calcd for $C_{21}H_{19}NO_4$: *m/z* = 188.0837; found: 188.0837 ± 2 ppm [M$^+$].

Ethyl 4-(1-*N*-benzyloxycarboyl-2-dihydroquinolyl)-4-ethyl-3-oxobutanoate (4k). Starting with **1** (0.26 g, 2.0 mmol, 1.0 equiv.), **2h** (1.21 g, 4.0 mmol, 2.0 Äquiv.), **3b** (0.41 g, 2.4 mmol, 1.2 equiv.), and 20 mL of CH$_2$Cl$_2$, **4k** was isolated by chromatography (silica gel, hexane/EtOAc = 10:1) as a yellow oil (0.237 g, 28%, mixture of diastereomers). ^{1}H-NMR (300 MHz, CDCl$_3$) δ = 0.79 – 0.89 (m, 3 H, CH$_3$), 1.25 – 1.39 (m, 2 H, CH$_2$), 3.34, 3.35 (2 x s, 3 H, CH$_3$), 4.15 – 4.26 (m, 2 H, CH$_2$), 4.90 (s, 1 H, CH, enol), 5.34 – 5.49 (m, 2 H, CH$_2$), 6.10 – 6.12 (m, 1 H, CH), 6.57 – 6.64 (m, 1 H, CH), 7.09 – 7.18 (m, 1 H, CH), 7.27 – 7.31 (m, 1 H, CH), 7.38 – 7.52 (m, 5 H, CH), 8.01 – 8.11 (m, 1 H, CH), 12.25 (s, 1 H, OH). ^{13}C-NMR (75 MHz, CDCl$_3$) δ = 12.0 (CH$_3$), 22.7 (CH$_2$), 40.1 (CH$_3$), 51.4 (CH$_2$), 60.1 (CH), 68.1 (CH$_2$), 121.7, 124.9, 126.1, 126.9 (CH), 127.6 (C), 128.0, 128.1, 128.3, 128.4, 128.4, 128.5, 128.5, 128.9 (CH), 135.5, 152.0, 166.5, 205.3 (C). IR (KBr): $\tilde{\nu}$ = 3067 (w), 3035 (w), 2968 (m), 2936 (m), 2878 (w), 1712 (s), 1652 (s), 1489 (s), 1457 (s). MS (EI, 70 eV): *m*/*z* (%) = 285 (24). UV (λ, log ε): 205.99 (4.3), 235.92

(4.2). Anal. Calcd for $C_{25}H_{27}NO_5$: C, 71.24; H, 6.46; N, 3.32. Found: C, 71.14; H, 6.01; N, 3.09.

Ethyl 4-(1-*N*-benzyloxycarboyl-2-dihydroquinolyl)-4-ethyoxy-3-oxobutanoate (4l). Starting with **1** (0.26 g, 2.0 mmol, 1.0 equiv.), **2i** (1.27 g, 4.0 mmol, 2.0 equiv.), **3b** (0.41 g, 2.4 mmol, 1.2 equiv.), and 20 mL of CH_2Cl_2, **4l** was isolated (silica gel, hexane/EtOAc = 10:1) as a yellow oil (0.400 g, 46%, mixture of diastereomers). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.95 – 1.05$ (t, $^3J = 7.0$ Hz, 3 H, CH_3), 1.23 – 1.35 (m, 2 H, CH_2), 3.29 – 3.62 (m, 5 H, CH_2, CH_3), 4.14 – 4.19 (m, 2 H, CH_2), 4.70 (s, 1 H, CH, enol), 5.28 – 5.38 (m, 2 H, CH_2), 5.96 (q, 1 H, CH), 6.58 – 6.61 (m, 1 H, CH), 7.07 – 7.09 (m, 1 H, CH), 7.10 – 7.17 (m, 1 H, CH), 7.27 – 7.39 (m, 5 H, CH), 8.01 – 8.05 (m, 1 H, CH), 12.55 (s, 1 H, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 13.9$, 14.0, 14.7, 14.8 (CH_3), 41.4, 41.5 (CH), 45.5, 45.7 (CH_2), 46.4, 46.7 (CH_2), 53.3 (CH), 61.1, 61.1 (CH_2), 67.6, 67.7 (CH_2), 84.9 (CH), 89.3 (CH), 97.6 (CH), 106.9 (CH), 122.8, 124.2, 124.6, 126.1, 126.5, 127.7, 127.8, 127.9, 128.0, 128.6, 128.9, 129.1 (CH), 135.7, 152.1, 166.9, 173.8, 203.5 (C). UV-Vis (λ, log ε): 204.32 (4.4), 236.88 (4.3). IR (KBr): $\tilde{\nu} = 3066$ (w), 3035 (w), 2979 (m), 2936 (m), 2899 (w), 2877 (w), 1655 (s), 1499 (s), 1454 (m). MS (EI, 70 eV): *m*/*z* (%) = 438 (M^+, 4), 262 (14), 220 (19), 91 (100), 29 (13). Anal. Calcd for $C_{25}H_{27}NO_6$: C, 68.64; H, 6.22; N, 3.20. Found: C, 68.64; H, 6.22; N, 3.20.

Ethyl 4-(1-(*N*-methoxycarbonyl–4-dihydropyridyl)-3-oxobutanoate (6a). Starting with **5** (0.16 g, 2.0 mmol, 1.0 equiv.), **2a** (1.09 g, 4.0 mmol, 2.0 equiv.), **3a** (0.23 g, 2.4 mmol, 1.2 equiv.), and 20 mL of CH_2Cl_2, **6a** was isolated by chromatography (silica gel, hexane/EtOAc = 7:1) as a red oil (0.115 g, 22%). ^{1}H-NMR (300 MHz, $CDCl_3$) $\delta = 1.33$ (t, $^3J = 7.0$ Hz, 3 H, CH_3), 2.66 (d, $^3J = 7.0$ Hz, 2 H, CH_2), 3.42 - 3.52 (m, $^3J = 8.0$ Hz, 2 H, CH_2, keto), 3.77, 3.79 (2 x s, 3 H, CH_3), 4.16 - 4.23 (q, $^3J = 7.0$ Hz, 2 H, CH_2), 4.84 - 4.87 (m, 1 H, CH), 5.03 (s, 1 H, CH, enol), 6.71 - 6.84 (m, 2 H, CH), 7.15 - 7.17 (m, 1 H, CH), 8.57 - 8.59 (m, 1 H, CH), 12.01 (s, 1 H, OH). Due to the instability of the compound, a ^{13}C-NMR spectrum could not be obtained. UV-Vis (λ, log ε): 228.96 (4.1). IR (KBr): $\tilde{\nu} = 2984$ (w), 2960 (w), 1722 (s), 1696 (s), 1654 (m), 1636 (m), 1445 (s). MS (EI, 70 eV): *m*/*z* (%) = 267 (M^+, 7), 221 (31), 138 (93), 94 (40), 93 (100). Anal. Calcd for $C_{13}H_{17}NO_5$: C, 58.42; H, 6.41; N, 5.24. Found: C, 58.77; H, 6.39; N, 5.36.

Methyl 4-(1-(*N*-methoxycarbonyl–4-dihydropyridyl)-3-oxobutanoate (6b). Starting with 5 (0.16 g, 2.0 mmol, 1.0 equiv.), CH_2Cl_2 (20 mL), **2b** (4.0 mmol, 2.0 equiv.) and **3a** (0.23 g, 2.4 mmol, 1.2 equiv.), **6b** was isolated by chromatography (silica gel, hexane/EtOAc = 7:1 → 5:1) as a red oil (0.107 g, 21%). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 2.65$ (d, $^3J = 7.0$ Hz, 2 H, CH_2), 3.38 - 3.52 (m, 2 H, CH_2, keto), 3.73, 3.74 (2 x s, 3 H, CH_3, keto, enol), 3.80, 3.83 (2 x s, 3 H, CH_3), 4.84 - 4.87 (m, 1 H, CH), 4.99 (s, 1 H, CH, enol), 6.72 - 6.83 (m, 2 H, CH), 7.15 - 7.17 (m, 1 H, CH), 8.57 - 8.59 (m, 1 H, CH), 12.02 (s, 1 H, OH). Due to the instability of the compound, a ^{13}C-NMR spectrum could not be obtained. UV-Vis (λ, log ε): 229.41 (4.1). IR (KBr): $\tilde{\nu}$ = 2957 (w), 1695 (s), 1660 (w), 1634 (m), 1444 (s). MS (EI, 70 eV): *m/z* (%) = 253 (M^+, 17), 252 (100), 178 (39), 150 (90), 101 (66). Anal. Calcd for $C_{12}H_{15}NO_5$: C, 56.91; H, 5.97; N, 5.53. Found: C, 56.54; H, 5.34; N, 5.53.

Methoxyethyl 4-(1-(*N*-methoxycarbonyl–4-dihydropyridyl)-3-oxobutanoate (6c). Starting with **5** (0.316 g, 4.0 mmol), **3a** (0.568 g, 6.0 mmol), and **2d** (2.430 g, 8.0 mmol), **6c** was isolated as a yellow oil (0.241 g, 20%, keto/enol = 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.50 (d, ^3J = 7.0 Hz, 1 H, CH), 3.16 – 3.19 (m, 3 H, CH, CH_2, keto, enol), 3.30 (s, 3 H, CH_3, enol), 3.32 (s, 3 H, CH_3, keto), 3.30-3.43 (m, 2 H, CH_2, keto, enol), 3.58 (s, 3 H, CH_3, enol), 3.60 (s, 3 H, CH_3, keto), 4.07 – 4.10 (m, 2 H, CH_2, keto, enol), 4.58-4.75 (m, 2 H, CH, keto), 4.86 (s, 1 H, CH, enol), 4.89 – 5.19 (m, 1 H, CH, enol), 5.39 – 5.81 (m, 1 H, CH, enol), 6.39 – 6.69 (m, 1 H, CH, keto), 11.81 (s, 1 H, OH, enol). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.6, 30.2 (CH, keto, enol), 49.2, 49.5 (CH_2, keto, enol), 51.2 (CH_2, keto), 53.0, 53.1, 58.4, 58.5 (CH_3, keto, enol), 63.8, 63.9, 69.9, 70.0 (CH_2, keto, enol), 89.3 (CH, enol), 108.2, 108.7, 122.4, 122.6 (CH, keto, enol), 151.98, 150.99, 166.3, 166.5, 171.6, 200.2 (C, keto, enol).

Ethyl 4-(1-(*N*-benzyloxycarbonyl–4-dihydropyridyl)-3-oxobutanoate (6d). Starting with **5** (0.16 g, 2.0 mmol, 1.0 equiv.), **2a** (1.09 g, 4.0 mmol, 2.0 equiv.), **3b** (0.41 g, 2.4 mmol, 1.2 equiv.), and 20 mL of CH_2Cl_2, **6d** was isolated by chromatography (silica gel, hexane/EtOAc = 10:1) as a red oil (0.453 g, 66%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.28 (t, ^3J = 7.0 Hz, 3 H, CH_3), 2.65 (d, ^3J = 7.0 Hz, 2 H, CH_2), 3.41 (s, 1 H, CH), 3.47 (q, ^3J = 9.0 Hz, 2 H, CH_2), 4.16 - 4.23 (m, 2 H, CH_2,), 4.83 - 4.90 (m, 1 H, CH), 5.19 - 5.27 (m, 2 H, CH_2), 5.29 (s, 1 H, CH, enol), 5.90 - 5.96 (m, 1 H, CH), 6.76 - 6.86 (m, 2 H, CH), 7.30 - 7.38 (m, 5 H, CH). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 28.3 (CH), 49.9 (CH_2), 51.7 (CH_2), 61.5 (CH_2), 68.2 (CH_2), 124.8, 126.8 (CH), 127.4 (C), 127.9, 128.0, 128.1 (CH), 135.5, 166.8, 200.7 (C). IR (KBr) $\tilde{\nu}$ = 3466 (w), 3442 (w), 3065 (w), 3035 (w), 2983 (m), 2938 (w), 2905 (w), 1650 (m), 1638 (m), 1583 (w), 1498 (w), 1451 (m). MS (EI, 70 eV): *m/z* = 343 (M^+, 2), 170 (14), 93 (24), 92 (16), 91 (100). Anal. Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16; N, 4.08. Found: C, 65.40; H, 5.93; N, 3.98.

Methyl 4-(1-(*N*-benzyloxycarbonyl–4-dihydropyridyl)-3-oxobutanoate (6e). Starting with **5** (0.16 g, 2.0 mmol, 1.0 equiv.), **2b** (1.04 g, 4.0 mmol, 2.0 equiv.) and **3b** (0.41 g, 2.4 mmol, 1.2 equiv.), and 20 mL of CH_2Cl_2, **6e** was isolated by chromatography (silica gel, hexane/EtOAc = 7:1) as a red oil (0.414 g, 63%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.64 (d, ^3J = 7 Hz, 2 H, CH_2), 3.42 - 3.52 (m, 2 H, CH_2, keto), 3.72, 3.73 (2 x s, 3 H, CH_3, keto, enol), 4.82 - 4.92 (m, 1 H, CH), 5.19 - 5.26 (m, 2 H, CH_2), 5.29 (s, 1 H, CH, enol), 5.90 - 5.95 (m, 1 H, CH), 6.68 - 6.86 (m, 2 H, CH), 7.30 - 7.41 (m, 5 H, CH), 12.01 (s, 1 H, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 28.2 (CH), 49.2 (CH_2), 51.5 (CH_2), 52.3 (CH_3), 68.1 (CH_2), 124.9, 126.9 (CH), 127.5 (C), 128.1, 128.2, 128.6 (CH), 135.5, 167.3, 200.7 (C). UV-Vis (λ, log ε): 207.79 (4.0). IR (KBr): $\tilde{\nu}$ = 1746 (m), 1715 (s), 1651 (w), 1635 (w). MS (EI, 70 eV): *m/z* (%) = 329 (M^+, 1), 214 (6), 170 (16), 92 (17), 91 (100). Anal. Calcd for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.81; N, 4.25. Found: C, 63.88; H, 5.24; N, 4.00.

1-(1-*N*-Methoxycarboyl-4-dihydropyridyl)-2,4-dioxopentane (6f). Starting with **5** (0.119 g, 1.5 mmol), **3a** (0.213 g, 2.3 mmol), and **2f** (0.732 g, 3.0 mmol), **6f** was isolated as a yellow oil (0.126 g, 35%, keto/enol = 3:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.07 (s, 3 H, CH_3), 2.36 (d, ^3J = 7.0 Hz, 2 H, CH_2), 3.43 (m, 1 H, CH), 3.57 (s, 2 H, CH_2, keto), 3.77 (s, 3 H, CH_3), 4.82 - 4.91 (m, 2 H, CH), 5.48 (s, 1 H, CH, enol), 6.68 – 6.85 (m, 2 H, CH), 15.43 (br, 1 H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0 (CH_3), 30.1 (CH), 47.2 (CH_2), 52.3 (CH_2, keto), 53.3 (CH_3), 100.9 (CH, enol), 108.5, 108.9, 123.2, 123.2 (CH, keto, enol), 151.7, 190.5, 191.7 (C). IR (KBr): $\tilde{\nu}$ = 3437 (w), 2958 (m), 2923 (w), 1725 (s), 1697 (s), 1630 (s), 1610 (s), 1444 (s), 1417 (m) cm^{-1}. UV-Vis (MeCN): λ_{max} (lg ε) = 228.52 (4.03) nm. MS (EI, 70 eV): *m/z* = 237 (M^+, 10), 138 (100), 94 (62), 84 (32), 60 (14). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 61.09; H, 6.71; N, 5.52.

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