Synthesis of Coumarins and Quinolones by Intramolecular Aldol Condensation Reactions of Titanium Enediolates

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Dedicated to Prof. Dr. Dr. h.c. mult. Günther Wilke on the occasion of his 70th birthday

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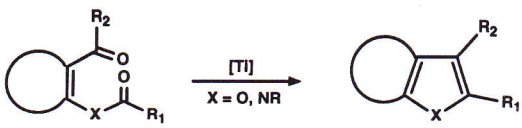
Low-Valent Titanium, Enediolates, Coumarins, 2-Quinolones, Aldol Condensation

Low-valent titanium prepared by the reduction of $TiCl_3$ with zinc dust oxidatively adds to α-ketoamides or α-ketoesters with the formation of the corresponding titanium enediolates. These 1,2-difunctional nucleophiles, which have hardly been used in organic synthesis so far, undergo regioselective intramolecular aldol condensation reactions with various electrophiles such as aldehydes, ketones, nitriles, esters and amides. This methodology allows the synthesis of differently substituted coumarin and 2-quinolone derivatives.

Low-valent titanium [Ti] prepared by the reduction of $TiCl_x$ (x = 3, 4) with various reducing agents is a versatile tool for organic synthesis. Due to its high oxophilicity and electron transfer ability it promotes *i.a.* the reductive coupling of aldehydes or ketones to olefins, generally referred to as "McMurry reaction" [1]. A pronounced template effect of the titanium species makes the cyclization of dicarbonyl compounds particularly favourable and allows the formation of cycloalkenes independent of the ring size. These specific features are responsible for the widespread applications of this reaction in the synthesis of natural and non-natural products [1].

Its most important short-coming, however, stems from the limitation to aldehydes and ketones as essentially the only substrates that undergo such reductive C–C bond formations [1]. Only recently we have been able to extend the scope of titanium-promoted processes beyond these traditional starting materials. Intramolecular alkylidenations of esters or amides as depicted in Scheme 1 give a ready access to the furan, pyrrole, benzo[b]furan and indole series [2–4]. In pursuing this concept, we now describe a complementary approach to six-membered heterocycles based upon the oxidative addition of low-valent titanium to 1,2-dicarbonyl compounds.



Scheme 1.

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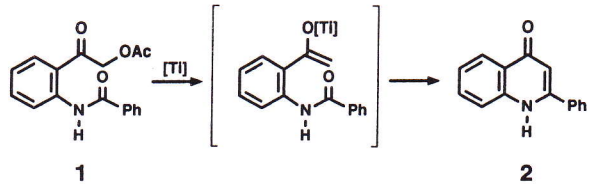
Results and Discussion

It is well established that activated titanium [Ti] readily deoxygenates acyloin derivatives most likely *via* the respective titanium enolates [2a, 5]. Although early attempts to trap these intermediates had failed [5], we were able to intercept one of them in an entropically favoured intramolecular way leading to the formation of the 4-quinolone **2** from substrate **1** (Scheme 2) [4].



1 **2**

Scheme 2.

Although the reactivity of 1,2-dicarbonyl compounds might by closely tied to that of acyloins titanium-mediated transformations of this group of substrates have been even less studied. There is some precedence in the literature that they afford the respective enediolates upon treatment with low-valent metals (Scheme 3). As early as 1972,

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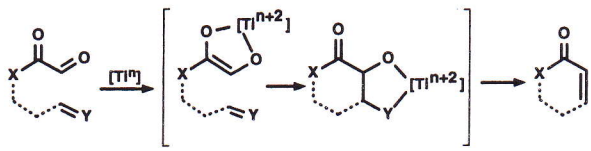
Floriani *et al.* reported a successful oxidative addition of $Cp_2Ti(CO)_2$ to 9,10-phenanthrenequinone [6]. Schobert *et al.* have later on extended this chemistry to other vicinal diketones and derivatives thereof using "reactive titanocene" (formed by reduction of Cp_2TiCl_2 with Mg) as the reagent. The 1,2-difunctional nucleophiles thus obtained were trapped with strong electrophiles such as H^+, phosgene, $PhBCl_2$, $PhPCl_2$ and acid chlorides [7]. Similarly, α-ketoesters have been used in low-valent titanium-mediated aldol reactions [8].



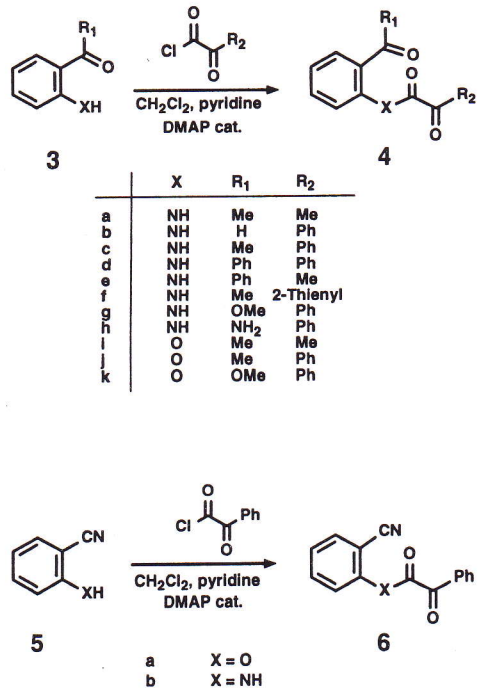
Scheme 3.

We intended to devise intramolecular versions of such reactions (Scheme 3). Being entropically biased, they might allow to intercept the titanium enediolates with less reactive electrophilic groups such as aldehydes, ketones, esters, amides or nitriles.

A set of suitable substrates **4a–k** and **6a, b** was prepared by the acylation of commercially available compounds **3** and **5** with different α-ketoacid chlorides [9] under standard conditions (Scheme 4, Table II). In case of X = O only moderate yields have been obtained because of the low nucleophilicity of the phenolic –OH and of partial hydrolysis of the esters **4i, j** and **6a** during flash chromatography.

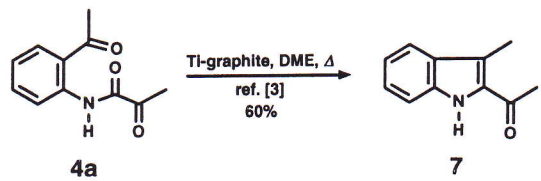
In a previous study [3] we reported the cyclization of substrate **4a** to the simple indole alkaloid salvadoricine **7** in 60% yield as the only product that could be isolated from the crude reaction mixture (Scheme 5). The striking chemoselectivity of this transformation in favour of the ketone-amide rather than the conventional ketone–ketone coupling process together with the complete resistance of the carbonyl group of **7** to an excess of the titanium reagent used are without precedence in the literature.

This result, however, turned out to be an exception to the rule, since all other substrates of this series followed a different pathway as can be seen from the data compiled in Table I. Thus, compounds **4b–f** readily cyclized to the corresponding



	X	R_1	R_2
a	NH	Me	Me
b	NH	H	Ph
c	NH	Me	Ph
d	NH	Ph	Ph
e	NH	Ph	Me
f	NH	Me	2-Thienyl
g	NH	OMe	Ph
h	NH	NH_2	Ph
i	O	Me	Me
j	O	Me	Ph
k	O	OMe	Ph

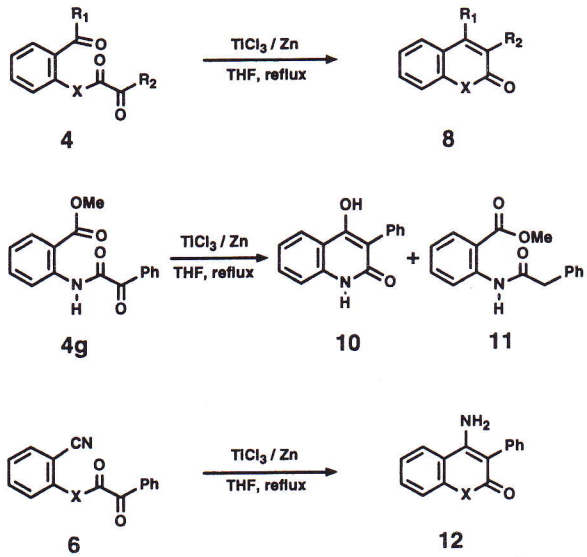
Scheme 4.



Scheme 5.

2-quinolone derivatives **8b–f** in good yields (Scheme 6). Indoles were not observed, except in the case of substrate **4c** where a minute amount of 2-benzoyl-3-methylindole (≈5%) accompanied the formation of quinolone **8c.** Similarly, esters **4i, j** afforded the corresponding 3,4-disubstituted coumarins **8i, j** without incident (Scheme 6).

Entries 6, 7, 10–13 in Table I comprise those cases in which we tried to intercept the intermediate enediolates with electrophilic groups other than an aldehyde or a ketone. An adjacent ester or a carboxylic acid amide group were only partly suitable for this purpose. Compound **4g** gave a



Scheme 6.

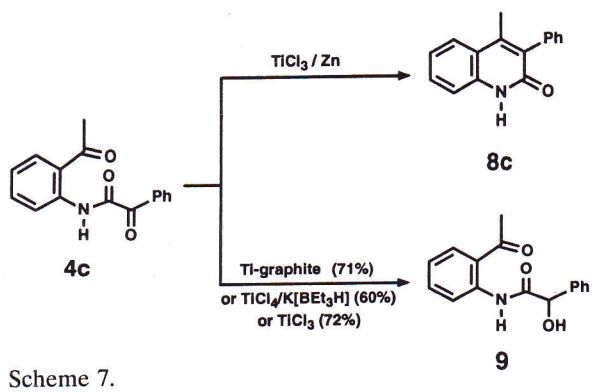
Table I. Low-valent titanium-induced 2-quinolone and coumarin syntheses. Method **A:** $TiCl_3$ was reduced with Zn-dust prior to the addition of the substrate [14]; Method **B:** reduction of $TiCl_3$ with Zn-dust in the presence of the substrate [4] (*cf.* Experimental section).

Entry	Substrate	Method	Reaction time [h]	Product [yield %]
1	**4b**	A	5	**8b** (64%)
2	**4c**	A	1	**8c** (80%)[a]
3	**4d**	A	16	**8d** (68%)
4	**4e**	A	16	**8e** (69%)
5	**4f**	A	16	**8f** (50%)
6	**4g**	B	3	**10** (41%), **11** (15%)
7	**4h**	A	16	**12b** (40%)
8	**4i**	A	0.5	**8i** (80%)
9	**4j**	A	1	**8j** (76%)
10	**4k**	A	16	**3k** (79%)
11	**6a**	A	1	**12a** (85%)
12	**6a**	B	4	**12a** (86%)
13	**6b**	A	5	**12b** (45%).

[a] Together with 2-benzoyl-3-methylindole (≈5%).

mixture of the desired 4-hydroxy-2-quinolone **10** together with substantial amounts of the uncyclized deoxygenation product **11** [10]. Under the same conditions the phenylglyoxylate **4k** was cleaved to the parent methyl 2-hydroxybenzoate **3k.** A nitrile group, however, turned out to be suitable to trap the titanium enediolates, since compounds **6a, b** gave the 4-amino-substituted derivatives **12a, b** in reasonable to good yields (Table I, entries 11–13).

Remarkably, the results obtained proved to be highly dependent on the type of low-valent titanium [Ti] used. While in the salvadoricine synthesis titanium-graphite prepared by the reduction of $TiCl_3$ with potassium-graphite laminate (C_8K) [11] turned out to be suited best, this reagent failed to cyclize substrate **4c** but led to the simple reduction of the α-ketoamide group (Scheme 7). The formation of compound **9** may be explained *via* the protonation of an intermediate titanium enediolate during work-up. Ammonium ion stabilized titanium clusters obtained from $TiCl_4$/$K(BEt_3H)$ [12] gave the same product. $TiCl_3$ itself, which has previously been employed to mediate pinacol cross-coupling reactions of methyl phenylglyoxylate with aldehydes and ketones [13], also afforded **9** in comparable yield. In contrast, the titanium species prepared from $TiCl_3$ and zinc dust either prior to the addition of the substrate (method A) [14] or in its presence (method B) [4] promoted the desired condensation reactions and have therefore been used throughout this study.



Scheme 7.

These results highlight the empirical state of the art of low-valent titanium chemistry, where subtle changes in the reagent preparation may have great impact for the outcome of the reaction [1]. In view of the lack of reliable information on the actual nature of such "low-valent" titanium species an accurate interpretation of these results on a morphological basis is presently impossible [15].

Applications of these titanium-mediated reactions to the synthesis of heterocyclic natural products and of pharmacologically active compounds are in progress.

Experimental

All reactions were carried out in pre-dried glassware under argon using Schlenk techniques. Melting points were recorded on a Gallenkamp apparatus and are uncorrected. NMR: Bruker AM 200 at 200 MHz (^{1}H) and 50 MHz (^{13}C), respectively, in $CDCl_3$ with TMS as internal standard unless stated otherwise. MS: EI, Finnigan MAT 311 A (70 eV). IR: Nicolet FT-510. TLC: Polygram® Sil Gel/UV_{254} (Macherey, Nagel & Co.). Flash chromatography: Merck silica gel 60 (230–400 mesh) with hexane/ethyl acetate in various proportions as eluent. $TiCl_3$: Aldrich, 99%. Anhydrous solvents were obtained by distillation over the given drying agents: THF (potassium/benzophenone), DME (Na/K alloy), CH_2Cl_2 (CaH_2), pyridine (MS 4 Å). The 2-ketoacids were purchased from Aldrich and used without further purification. The corresponding acid chlorides have been prepared according to the literature [9].

Representative procedure for acylation reactions with 2-ketoacid chlorides

Phenylglyoxylic acid chloride (0.80 g, 4.74 mmol) [9] in CH_2Cl_2 (5 ml) was added dropwise to a solution of 2-hydroxybenzonitrile (0.50 g, 4.20 mmol) and a catalytic amount of 4-dimethylaminopyridine (*ca.* 50 mg) in CH_2Cl_2 (25 ml). The mixture was stirred at ambient temperature for 4 h, quenched with a saturated aqueous solution of $NaHCO_3$, the aqueous layer was extracted twice with CH_2Cl_2 (50 ml each), the combined organic phases were dried over Na_2SO_4, the solvent was evaporated and the residue was purified by flash chromatography with hexane/ethyl acetate (gradient 10/1 → 4/1) as eluent. All other α-ketoesters and α-ketoamides were prepared analogously. For yields, analytical and spectroscopic data see Table II.

General procedure for the formation of 2-quinolones and coumarins

Method A: A suspension of $TiCl_3$ (771 mg, 5.0 mmol) and zinc dust (653 mg, 10.0 mmol) in anhydrous THF (50 ml) was refluxed under Ar for 4 h. After a solution of the respective substrate (2.5 mmol) in THF (10 ml) was added rapidly to the boiling black mixture of the active titanium reagent, reflux was continued until TLC showed the complete conversion of the starting material. The reaction mixture was then allowed to cool to ambient temperature, filtered through a short pad of silica, the insoluble residue was washed with THF (≈30 ml) and ethyl acetate (≈50 ml) in several portions, the combined filtrates were evaporated and the residue chromatographed with hexane/ethyl acetate in various proportions. For the yields obtained and the reaction times see Table I. The analytical and spectroscopic data of the products (*cf.* Table I) are compiled below.

3-Phenyl-2-quinolone (**8b**)

M.p. 198–200 °C (dec.) (lit. 235 °C [16]). – IR (cm^{-1}): 2850–3250, 1660, 1570, 1495, 750, 700. – ^{1}H NMR (DMSO-d_6): δ = 11.94 (br s, 1H), 8.11 (s, 1H), 7.71–7.76 (m, 3H), 7.32–7.51 (m, 5H), 7.18 (dt, J = 0.6, 3.8, 1H). – ^{13}C NMR (DMSO-d_6): δ = 160.7, 138.0, 137.3, 135.9, 131.2, 129.8, 128.3, 127.8, 127.6, 127.4, 121.6, 119.2, 114.3. – MS: *m/z* (rel. intensity, %): 221 ([M$^+$], 100), 193 (7), 165 (15), 110 (8), 89 (8).

4-Methyl-3-phenyl-2-quinolone (**8c**)

M.p. 262–264 °C. – IR (cm^{-1}): 2750–3100, 1650, 1610, 1600, 1560, 1500, 1430, 1380, 1285, 980, 890, 750, 705. – ^{1}H NMR (DMSO-d_6): δ = 12.03 (br s, 1H), 7.86 (d, J = 8.5, 1H), 7.18–7.56 (m, 8H), 3.35 (s, 3H). – ^{13}C NMR (DMSO-d_6): δ = 161.0, 143.2, 137.8, 136.3, 132.0, 130.3, 130.0, 127.8, 127.1, 125.2, 121.7, 119.9, 115.1, 16.5. – MS: *m/z* (rel. intensity, %): 235 ([M$^+$], 67), 234 (100), 216 (14).

N-(2'-Acetylphenyl)-2-hydroxy-phenylacetamide (**9**)

IR (cm^{-1}): 2900–3500, 1655, 1580, 1530, 1455, 1250, 750. – ^{1}H NMR (DMSO-d_6): δ = 12.43 (br s, 1H), 8.60 (d, J = 8.4, 1H), 8.09 (dd, J = 1.5, 8, 1H), 7.18–7.63 (m, 7H), 6.81 (d, J = 4), 5.10 (d, J = 4, 1H), 3.39 (s, 3H). – ^{13}C NMR (DMSO-d_6): δ = 202.2, 172.1, 140.3, 138.9, 134.3, 132.1, 128.0, 127.5, 126.3, 122.7, 119.4, 73.9, 28.6. – MS: *m/z* (rel. intensity, %): 269 ([M$^+$], 10), 251 (49), 222 (9), 146 (34), 136 (100), 120 (54), 105 (17), 92 (16), 77 (22).

3,4-Diphenyl-2-quinolone (**8d**)

M.p. 303–305 °C (lit. 305–307 °C, 309–310 °C (EtOH) [17]). – IR (cm^{-1}): 2700–3200, 1645, 1595, 1570, 1500, 1485, 1440, 1430, 1375, 1290, 760, 700, 670, 650, 610, 560. – ^{1}H NMR (DMSO-d_6): δ = 12.10 (br s, 1H), 6.97–7.53 (14H). – ^{13}C NMR (DMSO-d_6): δ = 160.9, 147.8, 138.0, 135.8, 135.4, 131.7, 130.4, 129.8, 129.2, 127.7, 127.2, 126.8, 126.5, 126.3, 121.4, 119.6, 114.9. – MS: *m/z* (rel. intensity, %): 297 ([M$^+$], 59), 296 (100), 278 (17), 267 (10).

Table II. Analytical and characteristic spectroscopic data of the starting materials.

Compound	Yield [%]	m.p. [°C]	IR [cm^{-1}]	MS: *m/z* [%]	^1H NMR [δ]	^{13}C NMR [δ]
4b	71	120–122	3240, 1700, 1680, 1665	253 ([M^+], 12), 105 (100)	12.46 (br s, 1H, NH), 10.01 (s, 1H, CHO)	195.1, 186.9, 160.9
4c	88	107–108	3190, 1685, 1645	267 ([M^+], 6), 162 (100)	12.93 (br s, 1H, NH), 2.67 (s, 3H, –Me)	201.8, 186.7, 160.3, 28.0
4d	80	132.5–133.5	3270, 1690, 1670, 1640	329 ([M^+], 2), 224 (100)	12.11 (br s, 1H, NH)	198.4, 186.6, 159.9
4e	74	99–100	3240, 1690, 1630	267 ([M^+], 5), 224 (100)	11.90 (br s, 1H, NH), 2.55 (s, 3H, –Me)	198.6, 196.2, 158.7, 24.0
4f	75	149–150	3150, 1695, 1655	273 ([M^+], 7), 162 (100)	13.07 (br s, 1H, NH), 2.68 (s, 3H, –Me)	201.6, 177.6, 159.4, 28.0
4g	89	101–102	3440, 1710, 1680	283 ([M^+], 7), 146 (100)	12.44 (br s, 1H, NH), 3.92 (s, 3H, –OMe)	186.8, 167.8, 159.8, 52.4
4h	76	181–184	3400, 3190, 1690, 1660, 1610	268 ([M^+], 1), 163 (100)	12.88 (br s, 1H, NH), 8.34 (br s, 2H, NH_2)[c]	187.6, 170.1, 160.1[c]
4i	40	syrup	1770, 1740, 1685	206 ([M^+], 1), 121 (100)	2.60, 2.53 (s each, 3H, –Me)	196.5, 190.5, 158.6, 28.5, 26.2
4j	59	68–71	1750, 1690	105 (100)	2.58 (s, 3H, –Me)	196.8, 184.3, 160.8, 28.9
4k	89	59–61	1760, 1715, 1695	105 (100)[a]	3.83 (s, 3H, –OMe)	184.6, 164.6, 161.3, 52.3
6a	58	syrup	2240, 1760, 1690	105 (100)[b]	8.12–8.18 (m, 2H), 7.36–7.75 (m, 7H)	183.1, 159.6, 150.3, 114.0, 106.1
6b	81	106–108	3330, 2220, 1705, 1665	250 ([M^+], 9), 105 (100)	9.51 (br s, 1H, –NH)	185.4, 158.6, 115.3, 103.0

[a] Chemical ionization (NH_3): 302 ([$M+NH_4$]$^+$, 100%); [b] chemical ionization (NH_3): 269 ([$M+NH_4$]$^+$, 100%; [c] spectrum recorded in DMSO-d_6.

3-Methyl-4-phenyl-2-quinolone (**8e**)

M.p. 238–239 °C (lit. 238–239 °C [18]). – IR (cm^{-1}): 2800–3190, 1650, 1610, 1595, 1560, 1430, 1370, 1280, 1020, 755, 705, 670, 610. – ^1H NMR (DMSO-d_6): δ = 11.91 (br s, 1H), 7.20–7.58 (m, 7H), 7.01 and 6.85 (ddAB, J = 2, 6.6, 8.4, 2H), 3.35 (s, 3H). – ^{13}C NMR (DMSO-d_6): δ = 161.7, 146.7, 137.1, 136.3, 128.9, 128.5, 128.4, 128.0, 127.7, 126.8, 125.8, 121.2, 119.7, 114.8, 13.9. – MS: *m/z* (rel. intensity, %): 235 ([M^+], 56), 234 (100), 216 (16).

4-Methyl-3-(2'-thienyl)-2-quinolone (**8f**)

M.p. 263–265 °C. – IR (cm^{-1}): 2650–3180, 1640, 1600, 1555, 1505, 1435, 1385, 1280, 1235, 1160, 955, 940, 900, 850, 790, 780, 750, 735, 690, 660, 570. – ^1H NMR (DMSO-d_6): δ = 11.87 (br s, 1H), 7.79 (dd, J = 0.6, 4.2, 1H), 7.65 (dd, J = 0.6, 2.4, 1H), 7.51 (dt, J = 0.6, 3.8, 1H), 7.33 (dd, J = 0.4, 4.2, 1H), 7.22 (dt, J = 0.6, 3.8, 1H), 7.09–7.14 (m, 2H), 3.35 (s, 3H). – ^{13}C NMR (DMSO-d_6): δ = 159.8, 144.4, 136.9, 135.4, 129.7, 128.5, 126.5, 125.5, 124.9, 124.1, 121.3, 119.1, 114.5, 16.4. – MS: *m/z* (rel. intensity, %): 241 ([M^+], 100), 240 (53), 208 (14), 196 (7).

4-Hydroxy-3-phenyl-2-quinolone (**10**)

M.p. 318–320 °C (dec.) (lit. 320 °C [20]). – IR (cm^{-1}): 2700–3500, 1655, 1610, 1590, 1500, 1400, 1290, 1160, 1140, 760, 700, 555. – ^1H NMR (DMSO-d_6): δ = 11.47 (br s, 1H), 10.05 (br s, 1H), 7.91 (dd, J = 1.2, 8, 1H), 7.49 (dt, J = 1.0, 7, 1H), 7.24–7.42 (m, 6H), 7.16 (dt, J = 1.2, 7, 1H). – ^{13}C NMR (DMSO-d_6): δ = 162.4, 157.0, 137.7, 133.0, 130.9, 130.3, 127.4, 126.6, 122.8, 120.8, 115.2, 114.6, 112.4. – MS: *m/z* (rel. intensity, %): 237 ([M^+], 100), 120 (87), 92 (25).

N-(2'-Methoxycarbonylphenyl)-phenylacetamide (**11**)

Syrup. – IR (cm^{-1}): 3300, 3040, 2960, 1710, 1690, 1610, 1590, 1530, 1450, 1440, 1300, 1260, 1090. – ^1H NMR: δ = 11.05 (br s, 1H), 8.70 (dd, J = 1, 8.4, 1H), 7.97 (dd, J = 1.8, 7.8, 1H), 7.51 (dt, J = 1.6, 7.4, 1H), 7.20–7.40 (m, 5H), 7.05 (dt, J = 1.4, 7.4, 1H), 3.88 (s, 3H), 3.75 (s, 2H). – ^{13}C NMR: δ = 169.6, 168.0, 140.9, 134.0, 130.3, 129.1, 128.4, 126.8, 122.1, 120.0, 114.8, 107.4, 51.8, 45.5. – MS: *m/z* (rel. intensity, %): 269 ([M^+], 25), 178 (44), 151 (49), 146 (100), 119 (33), 91 (38), 65 (13).

4-Amino-3-phenyl-2-quinolone (**12b**)

M.p. 326–328 °C (dec.) (lit. 325 °C [19]). – IR (cm^{-1}): 3470, 3320, 2800–3250, 1630, 1610, 1595, 1510, 1415, 755, 700. – ^1H NMR (DMSO)-d_6): δ = 11.04 (s, 1H), 8.00 (d, J = 4, 1H), 7.24–7.46 (m, 7H), 7.10 (t, J = 3.6, 1H), 5.86 (br s, 2H). – ^{13}C NMR (DMSO-d_6): δ = 161.3, 148.1, 138.0, 134.8, 130.7, 129.7, 128.1, 126.3, 122.9, 120.2, 114.8, 113.2, 105.7. – MS: *m/z* (rel. intensity, %): 236 ([M^+], 66), 235 (100), 217 (20).

Representative procedure for the "instant" preparation of coumarins by method B

A suspension of $TiCl_3$ (771 mg, 5.0 mmol), zinc dust (653 mg, 10.0 mmol) and substrate **6a** (630 mg, 2.51 mmol) in THF (30 ml) was refluxed under Ar for 4 h until TLC showed complete conversion of the starting material. After cooling to room temperature the mixture was filtered through a short pad of silica, the inorganic residue was washed with ethyl acetate (≈ 50 ml) in several portions, the filtrate was evaporated and the residue chromatographed with hexane/ethyl acetate (gradient 4/1 → 1/1) as eluent. Thus, product **12a** was obtained as pale-yellow crystals (510 mg, 86%).

3,4-Dimethylcoumarin (**8i**)

M.p. 110–111 °C (lit. 112–114 °C [21]). – IR (cm^{-1}): 2850–3050, 1705, 1625, 1600, 1490, 1460, 1380, 1290, 1150, 1090, 780, 760, 730. – ^1H NMR: δ = 7.20–7.59 (m, 4H), 2.41 (s, 3H), 2.21 (s, 3H). – ^{13}C NMR: δ = 161.5, 151.5, 145.5, 129.9, 123.8, 123.6, 121.8, 120.1, 116.2, 14.5, 13.0. – MS: *m/z* (rel. intensity, %): 174 ([M^+], 100), 146 (30), 131 (46).

4-Methyl-3-phenylcoumarin (**8j**)

M.p. 144–146 °C (lit. 156 °C [22]). – IR (cm^{-1}): 3060, 2940, 1715, 1620, 1610, 1490, 1450, 1380, 1300, 1180, 1150, 1080, 965, 750, 705. – ^1H NMR: δ = 7.66 (dd, J = 1.6, 8, 1H), 7.23–7.56 (m, 8H), 2.32 (s, 3H). – ^{13}C NMR: δ = 160.5, 152.3, 147.2, 134.0, 130.9, 129.6, 128.0, 127.9, 127.8, 124.7, 123.8, 120.1, 116.4, 16.1. – MS: *m/z* (rel. intensity, %): 236 ([M^+], 100), 235 (65), 208 (37), 207 (49), 178 (21), 131 (20), 89 (14), 77 (8).

4-Amino-3-phenylcoumarin (**12a**)

M.p. 179–180 °C (lit. 182 °C [23]). – IR (cm^{-1}): 3430, 3340, 3250, 1735, 1625, 1610, 1590, 1575, 1525, 1440, 1290, 1250, 1220, 755, 705. – ^1H NMR (DMSO-d_6): δ = 8.15 (dd, J = 8.6, 1.7, 1H), 7.25–7.65 (m, 8H), 6.75 (br s, 2H). – ^{13}C NMR (DMSO-d_6): δ = 160.7, 152.4, 150.6, 133.6, 131.7, 130.8, 128.4, 127.0, 123.4, 123.2, 116.3, 114.4, 97.4. – MS: *m/z* (rel. intensity, %): 237 ([M^+], 100), 236 (61), 209 (26), 180 (28), 165 (10), 120 (16), 90 (14), 77 (11).

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