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Reductive coupling of hydantoins with benzophenones by low-valent titanium: Synthesis of 4-substituted 1*H*-imidazol-2(3*H*)-ones and unusual two-to-two coupled products

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ABSTRACT

The reductive coupling of 1,3-dimethyhydantoin with benzophenones by $TiCl_4$ -Zn in THF gave 4diarylmethyl-1*H*-imidazol-2(3*H*)-ones as four-electron reduced one-to-one coupled products and their dimers as two-to-two coupled products predominantly by controlling the reaction conditions. The reductive coupling of 5-alkyl-1,3-dimethyhydantoins with benzophenones produced 5-alkyl-4diarylmethyl-1*H*-imidazol-2(3*H*)-ones as the sole products irrespective to the reaction conditions. On the other hand, the reductive coupling of 1,3-dimethyhydantoin with cyclic benzophenones selectively 4arylhydroxymethyl-1*H*-imidazol-2(3*H*)-ones as two-electron reduced one-to-one coupled products and they were further reduced to 4-diarylmethyl-1*H*-imidazol-2(3*H*)-ones.

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1. Introduction

Reductive cross-coupling between two different carbonyl compounds is one of the useful means for carbon-carbon bond formation.¹ For this purpose, a variety of methods have been reported using metal reducing agents, such as low-valent titanium² and SmI_2 ³ and electroreduction.⁴ Of these, the reductive cross-coupling using low-valent titanium is well known as Cross McMurry coupling.^{2,5} In our recent reports, we disclosed that Cross McMurry coupling is a powerful tool for the reductive coupling of heterocycles, such as uracils,^{6a} *N*-methoxycarbonyl lactams,^{6b} and aliphatic cyclic imides,^{6c} with benzophenones. In this paper, we report the reductive coupling of 1,3-dimethylhydantoins 1a-e with benzophenones **2a-g** by low-valent titanium generated from TiCl₄-Zn in THF (Schemes 1 and 2). Hydantoins are well known as α -amino acid analogs and have been actively studied due to their synthetic and pharmaceutical interest.⁷ However, the reductive coupling of hydantoins with carbonyl compounds has not been reported to date. Initially, we expected that 4-substituted 1H-imidazol-2(3H)-







ucts by the one-to-one reductive coupling of 5-unsubstituted hydantoin **1a** (R = H) with **2a-c** (Scheme 1). Unexpectedly, twoto-two coupled products 3 were formed predominantly by the reaction at 5-30 °C. The expected one-to-one coupled products 4 (R = H) could also be obtained mainly by the reaction at reflux temperature. On the other hand, 4,5-disubstituted **4** (R = alkyl) were the sole products in the reaction of 5-alkyl-1,3dimethylhydantoins **1b-e** (R = alkyl) with **2a-c**. In addition, twoelectron reduced products 5 were selectively obtained by the reaction of **1a** with cyclic benzophenones **2d-g** at 5–30 °C and the obtained **5** were further reduced to **4** by the treatment with TiCl₄-Zn at reflux temperature (Scheme 2). A variety of synthetic methods of substituted 1H-imidazol-2(3H)-ones have so far been reported, since these compounds attract significant interest as biologically active substances.^{8,9} This method provides a new synthetic route to 4-substituted and 4,5-disubstituted 1H-imidazol-2(3H)-ones **4** and **5** from readily available hydantoins, although the reduction of hydantoins to 4,5-unsubstituted 1H-imidazol-2(3H)ones with Cp₂Zr(H)Cl was reported.¹⁰ The reaction mechanism of the reductive coupling is also discussed.

ones 4 or 5 were obtained as four- or two-electron reduced prod-



Scheme 1. Reductive coupling of 1,3-dimethylhydantoins 1a-e with benzophenones 2a-c by Zn-TiCl₄.



Scheme 2. Reductive coupling of 1a with cyclic benzophenones 2d-g by Zn-TiCl₄.

2. Results and discussion

2.1. Reductive coupling of 1,3-dimethylhydantoins with benzophenones by TiCl₄/Zn

The results of the reductive coupling of 1,3-dimethylhydantoin (**1a**) with benzophenones **2a-c** are summarized in Table 1. First,

Table 1

Reductive coupling of **1a** with **2a-c** by TiCl₄-Zn.

the reaction of **1a** with benzophenone (**2a**) was carried out with the ratio of **1a/2a**/TiCl₄/Zn as 1/1/1/2 in THF at 5 °C for 2 h (run 1). After workup with 1 M HCl, unusual two-to-two coupled product **3a** was obtained in 37% yield as a mixture of *dl*- and *meso*-isomers (76:24). The both diastereomers of **3a** were separated by column chromatography and confirmed by X-ray crystallography. Since about 50% of **1a** was recovered in run 1, the amounts of **2a**, TiCl₄, and Zn for **1a**



run		mmol			temp.	time	% yield ^a			
		2	TiCl ₄	Zn			3	(dl:meso)	4	
1	2a	1	1	2	5 ° C	2 h	3a	37 (76:24)	4a	nd
2	2a	2	2	4	5 °C	2 h	3a	70 (76:24)	4a	4
3	2a	2	2	4	30 ° C	1 h	3a	56 (70:30)	4a	16
4	2a	2	4	8	30 ° C	1 h	3a	40 (65:35)	4a	31
5	2a	2	4	8	reflux	1 h	3a	15	4a	55 ^b
6	2a	2	4	16	reflux	1 h	3a	nd	4a	64 ^c
7	2b	2	2	4	5 °C	2 h	3b	52 (65:35)	4b	5
8	2b	2	2	4	30 ° C	1 h	3b	63 (57:43)	4b	7
9	2b	2	4	16	reflux	1 h	3b	nd	4b	54 ^d
10	2c	2	2	4	5 °C	2 h	3c	63 (55:45)	4c	12
11	2c	2	4	16	reflux	1 h	3c	trace	4c	43 ^e

^a Isolated yields. nd = not detected.

^b **6a** (12%) and **7a** (3%) were also obtained.

^c **6a** (18%) and **7a** (5%) were also obtained.

^d **6b** (10%) and **7b** (14%) were also obtained.

^e **6c** (17%) and **7c** (21%) were also obtained.



A

were doubled in run 2. The yield of **3a** increased to 70% and small amount (4%) of one-to-one adduct 4a was formed (run 2). When the reduction was carried out at 30 °C with the same ratio of reactants, the yield of **3a** decreased to 56% and **4a** was formed in 16% yield (run 3). By the reduction with the ratio of **1a/2a**/TiCl₄/Zn as 1/ 2/4/8 at 30 °C. the yield of **3a** further decreased to 40%, while that of **4a** increased to 31% (run 4). By the reduction with the same ratio at reflux temperature (run 5). 4a (55%) was vielded more than 3a (15%). Finally, the reaction was performed at reflux temperature in the presence of an excess amount (16 equiv) of Zn (run 6). As expected, 4a was obtained as the major product (64%), while 3a could not be detected. In this case, however, small amounts of two-to-one adducts 6a (12%) and 7a (3%) were also formed. In place of 2a, 4,4'difluorobenzophenone (2b) and 4,4'-dimethoxybenzophenone (2c) were employed as benzophenones and the similar results were afforded (runs 7-11). Two-to-two adducts 3b and 3c were formed predominantly by the reaction at 5–30 °C (runs 7, 8, and 10). On the contrary, one-to-one adducts 4b and 4c were obtained mainly under the reflux conditions, although the two-to-one adducts **6b,c** and **7b,c** were also formed (runs 9 and 11). Incidentally, the use of TiCl₃ instead of TiCl₄ resulted in the similar results, as previously reported in the early studies for the carbonyl-coupling reactions using low-valent titanium.² From the viewpoint of availability, TiCl₄ is much more preferable than TiCl₃ as a Ti source.

The reductive coupling of **1a** with cyclic benzophenones **2d-g** was carried out under the same conditions as those in Table 1 (Table 2). It is notable that two-electron reduced one-to-one adducts **5d-g** were the sole products at 5-30 °C in runs 1 and 3-7. At 30 °C, dehydrated product of **5d** (**8**, 21%) was formed to some extent (run 2), and further reduced product of **5g** (**4g**, 35%) was formed considerably (run 8). The obtained **5d-g** were reacted with TiCl₄ (2 eq)/Zn (4 eq) in THF at reflux temperature (Scheme 3). As expected from the result of run 2, dehydrated product **8** was obtained alone from **5d**. This result shows that the dehydration of **5d** proceeds more rapidly than the dehydroxylation of **5d**. On the other hand, dehydroxylated products **4e-g** were produced from **5e-g**, although prolonged reaction time (6–18 h) was required.

The reductive coupling of 5-alkyl-1,3-dimethylhydantoins **1b-e** with benzophenones **2a-c** by TiCl₄-Zn gave four-electron reduced

Table 2

Reductive coupling of 1a with 2d-g by TiCl₄-Zn.



Scheme 3. Reaction of 5d-g with TiCl₄-Zn.

one-to-one adducts **4h-m** as the sole products regardless of the reaction conditions (Table 3). The reactions of **1b** (R = Me) and **1c** (R = i-Bu) gave **4h-k** in moderate to good yields under the conditions with the ratio of **1/2**/TiCl₄/Zn as 1/2/2/4 (runs 1–6). However, the reaction of **1d** (R = Bn) with **2a** gave **4l** in a poor yield (33%) and more than 60% of **1d** was recovered under the same conditions (run 7). Therefore, the reaction was carried out with the ratio of **1/2**/TiCl₄/Zn as 1/5/5/10 to give **4l** in 60% yield (run 8). Even under the same conditions as in run 8, the reaction of **1e** (R = i-Pr) afforded **4m** in only 21% yield (run 9). These results show that the reductive coupling is strongly inhibited by the steric hindrance of the substituent at the 5-position in **1b-e**. In addition, bicyclic *N*-methylhydantoin **1f** derived from proline was also reacted with **2a-c** to give **4n-p** in moderate yields (Scheme 4).



run	2	Х	temp.	time	% yield of 5 ^a	
1	2d	CH ₂	5°C	3 h	5d	82
2	2d	CH ₂	30 °C	1 h	5d	58 ^b
3	2e	CH ₂ CH ₂	5 °C	3 h	5e	59
4	2e	CH ₂ CH ₂	30 °C	1 h	5e	60
5	2f	CH=CH	5 °C	3 h	5f	54
6	2f	CH=CH	30 °C	1 h	5f	68
7	2g	0	5 °C	2 h	5g	37
8	2g	0	30 ° C	1 h	5g	30 ^c

^a Isolated yields.

^b 8 (21%) was also obtained.

^c 4g (35%) was also obtained.

Table 3Reductive coupling of 1b-e with 2a-c by TiCl₄-Zn.



run	1	R	R				temp.	time	% yield of 4 ^a	
				2	TiCl ₄	Zn				
1	1b	Me	2a	2	2	4	5 °C	3 h	4h	72
2	1b	Me	2a	2	2	4	30 ° C	1 h	4h	87
3	1b	Me	2a	2	2	4	reflux	1 h	4h	78
4	1b	Me	2b	2	2	4	30 ° C	1 h	4i	65
5	1b	Me	2c	2	2	4	30 °C	1 h	4j	57
6	1c	<i>i</i> -Bu	2a	2	2	4	30 ° C	1 h	4k	63
7	1d	Bn	2a	2	2	4	30 ° C	1 h	41	33
8	1d	Bn	2a	5	5	10	30 ° C	1 h	41	60
9	1e	<i>i</i> -Pr	2a	5	5	10	30 ° C	1 h	4m	21

^a Isolated yields.



Scheme 4. Reductive coupling of 1f with 2a-c by TiCl₄-Zn.

2.2. Reductive coupling of 1,3-unsabstituted hydantoins with benzophenone by TiCl₄/Zn

Next, 1,3-unsubstituted hydantoins **9a-d** were employed as the substrates for the reductive coupling with **2a** (Table 4). Unfortunately, the reaction of **9a** (R = H) produced no coupled product with **2a**, since **9a** is mostly insoluble in THF even at elevated temperature (run 1). In contrast, 5-alkyl-hydantoins **9b-d** are soluble in THF at 30 °C and reacted with **2a** to give 4,5-disubstituted 1*H*-imidazol-2(3*H*)-ones **10b-d** in moderate yields (runs 2–6). Bicyclic hydantoin **9f** was also reacted with **2a** to give **10f** in 42% yield (Scheme 5).

2.3. Reaction mechanism of the reductive coupling

The presumed reaction mechanism of the reductive coupling of **1a** with **2** is illustrated in Scheme 6. Since **1a** is completely inert under the conditions for the reduction with TiCl₄-Zn, the reductive coupling is undoubtedly initiated by the reduction of **2**. First, dianion intermediate **A** is generated by two-electron transfer from low-valent titanium to **2**. The major by-products are the homo-coupled pinacols and its further reduced McMurry-type alkenes. For the cross coupling with **1a**, the nucleophilic attack of **A** at the 4-position of **1a** forms adduct **B**. The elimination of **B** to allylic alkoxide anion **C** and subsequent one-electron transfer to **C** occur

Table 4

Reductive coupling of **9a-c** with **2a** by $TiCl_4$ -Zn.



^a Isolated yields. nd = not detected.

rapidly to give allylic radical **D**. The dimerization of **D** at the 5-position proceeds predominantly under the conditions at 5-30 °C to produce two-to-two adduct **3**. On the contrary, the one-electron



Scheme 5. Reductive coupling of 9f with 2a by TiCl₄-Zn.



Scheme 6. Presumed reaction mechanism of reductive coupling of 1a with 2 by low-valent titanium.

transfer to **D** takes place more rapidly than the dimerization under the conditions at reflux temperature in the presence of an excess amount of Zn to give allylic anion **E**. One-to-one adduct **4** is formed by the protonation of **E** during work-up. The nucleophilic addition of **E** to **2** also proceeds under the reflux conditions to give **F** and **G**. Two-to-one adducts **6** and **7** are obtained from **F** and **G** after further two-electron transfer and following work-up. In the reactions of cyclic benzophenones **2d-g**, two-electron reduced one-to-one adduct **5d-g** were afforded selectively (Table 2), since the reduction of **C** to **D** is very slow at 5–30 °C. It is anticipated that the substitution by an alkyl group at the 5-position on **1a** inhibits the dimerization of **C**. Actually, the reaction of 5-alkylhydantoins **1b-f** with **2a-c** gave **4h-n** as the sole products regardless of the reaction conditions (Table 3 and Scheme 4). In the reactions of **1a** with **2a-c**, **C** seems to be the intermediate for the formation of **3a-c** and **4a-c**. Therefore, we tried to trap **5a-c** by stopping the reaction in an early



Scheme 7. Isolation of 5a,b and their reduction by TiCl₄-Zn.

stage. Consequently, small amounts of **5a** and **5b** could be isolated and their reactions with TiCl₄-Zn in THF at 5 °C gave **3a** and **3b**, respectively (Scheme 7). These results suggest that **C** is the intermediate for the formation of **3** and **4**.

3. Conclusion

In conclusion, the reductive coupling of 1,3-dimethylhydantoin (1a) with benzophenones 2a-c by TiCl₄-Zn predominantly gave two-to-two coupled products **3a-c** and one-to-one coupled products **4a-c** at 5–30 °C and reflux temperature, respectively. The reductive coupling of 1a with cyclic benzophenones 2d-g by TiCl₄-Zn at 5–30 °C selectively gave one-to-one coupled products 5d-g. The two-electron reduced adducts **5e-g** were further reduced by TiCl₄-Zn at reflux temperature to four-electron reduced adducts 4eg, while 5d was dehydrated to 8 under the same conditions. The reductive coupling of 5-alkyl-1,3-dimethylhydantoins 1b-e and bicyclic hydantoin 1f with 2a-c afforded 4h-p exclusively irrespective to the reaction conditions. In addition, 5-alkylhydantoins 9b-d,f also reductively coupled with 2a to give one-to-one coupled products 10b-d,f exclusively. Consequently, 5-substituted 1H-imidazol-2(3H)-ones (4a-c,e-g, 5d-g, and 8) and 4,5disubstituted 1H-imidazol-2(3H)-ones (4h-p and 10b-d,f) were effectively synthesized by the low-valent titanium mediated reductive coupling of hydantoins **1a-f** and **9b-d,f** with benzophenones 2a-g. This reductive coupling provides a promising method for the synthesis of new classes of 4-substituted and 4,5disubstituted 1H-imidazol-2(3H)-ones from readily available hydantoins.

4. Experimental section

4.1. General

Column chromatography was performed on silica gel 60. THF was freshly distilled from sodium benzophenone ketyl. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were measured on a JEOL JNM-ECP500 spectrometer with tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a Shimadzu IRAffinity-1 infrared spectrometer. HRMS were measured on a Thermo Scientific Exactive FTMS spectrometer. Elemental analyses

were recorded on an Elementar Vario EL III elemental analyzer. Melting points were uncorrected.

4.2. Starting materials

Hydantoin (**9a**) is commercially available. 5-Alkylhydantoins **9b-e** and **9f** were prepared from dl- α -amino acids and KOCN according to the reported method.¹¹

4.3. Methylation of hydantoins

A mixture of **9a** (3.0 g, 30 mmol), MeI (12.8 g, 90 mmol), and K₂CO₃ (12.4 g, 90 mmol) in CH₃CN (20 mL) was refluxed for 24 h. After the solvent was removed *in vacuo*, the residue was dissolved in ethyl acetate (50 mL) and then the insoluble solid was filtered off. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel to give **1a**. The 1,3-dimethylhydantoins **1a-c** are known.^{12–14}

4.3.1. 1,3-Dimethylimidazolidine-2,4-dione $(1a)^{12}$

Colorless paste; *Rf* 0.3 (ethyl acetate-ethanol, 1:1); ¹H NMR (CDCl₃) δ 3.01 (s, 3H), 3.03 (s, 3H), 3.87 (s, 1H); ¹³C NMR (CDCl₃) δ 24.5 (q), 29.3 (q), 51.4 (t), 156.7 (s), 169.7 (s).

4.3.2. 1,3,5-Trimethylimidazolidine-2,4-dione (**1b**)¹³

Colorless paste; *Rf* 0.35 (ethyl acetate-ethanol, 1:1); ¹H NMR (CDCl₃) δ 1.43 (d, 3H, *J* = 7.0 Hz), 2.96 (s, 3H), 3.02 (s, 3H), 3.87 (q, 2H, *J* = 7.0 Hz); ¹³C NMR (CDCl₃) δ 14.6 (q), 24.5 (q), 27.1 (q), 56.9 (d), 156.1 (s), 173.4 (s).

4.3.3. 5-Isobutyl-1,3-dimethylimidazolidine-2,4-dione (1c)¹⁴

Colorless paste; *Rf* 0.35 (ethyl acetate-ethanol, 2:1); ¹H NMR (CDCl₃) δ 0.93 (d, 3H, *J* = 6.9 Hz), 0.96 (d, 3H, *J* = 6.6 Hz), 1.67–1.76 (m, 2H), 1.86–1.95 (m, 1H), 2.96 (s, 3H), 3.01 (s, 3H), 3.84 (t, 1H, *J* = 5.7 Hz); ¹³C NMR (CDCl₃) δ 22.4 (q), 22.9 (q), 24.1 (d), 28.0 (q), 38.0 (t), 59.9 (d), 156.6 (s), 173.3 (s).

4.3.4. 5-Benzyl-1,3-dimethylimidazolidine-2,4-dione (1d)

White solid; *Rf* 0.4 (hexanes-ethyl acetate, 1:1); mp 74–75 °C; IR (ATR) 1755, 1688 cm⁻¹; ¹H NMR (CDCl₃) δ 2.86 (s, 3H), 2.90 (s, 3H), 3.13 (dd, 1H, *J* = 4.9, 14.5 Hz), 3.21 (dd, 1H, *J* = 4.9, 14.5 Hz), 4.11 (t,

1H, J = 4.9 Hz), 7.12–7.16 (m, 2H), 7.22–7.30 (m, 3H); ¹³C NMR (CDCl₃) δ 24.5 (q), 28,4 (q), 35.2 (t), 62.5 (d), 127.2 (d), 128.5 (d), 129.1 (d), 134.5 (s), 156.6 (s), 172.2 (s); HRMS (ESI) calcd for C₁₂H₁₅N₂O₂ (M + H⁺) 219.1134; found 219.1129.

4.3.5. 5-Isopropyl-1,3-dimethylimidazolidine-2,4-dione (1e)

Colorless paste; *Rf* 0.55 (hexanes-ethyl acetate, 1:1); IR (ATR) 1769, 1697 cm⁻¹; ¹H NMR (CDCl₃) δ 0.93 (d, 3H, *J* = 7.0 Hz), 1.13 (d, 3H, *J* = 7.0 Hz), 2.22–2.32 (m, 1H), 2.97 (s, 3H), 3.00 (s, 3H), 3.72 (d, 1H, *J* = 2.9 Hz); ¹³C NMR (CDCl₃) δ 16.5 (q), 17.0 (q), 24.4 (q), 28.2 (q), 28.5 (d), 66.1 (d), 156.9 (s), 172.1 (s); HRMS (ESI) calcd for C₈H₁₅N₂O₂ (M + H⁺) 171.1134; found 171.1131.

4.3.6. 2-Methyltetrahydro-1H-pyrrolo[1,2-c]imidazole-1,3(2H)dione (1f)

Colorless paste; *Rf* 0.35 (hexanes-ethyl acetate, 1:1); IR (ATR) 1773, 1694 cm⁻¹; ¹H NMR (CDCl₃) δ 1.67–1.75 (m, 1H), 2.01–2.14 (m, 2H), 2.22–2.30 (m, 1H), 3.00 (s, 3H), 3.23–3.29 (m, 1H), 3.66–3.72 (m, 1H), 4.10 (dd, 1H, *J* = 7.9, 9.0 Hz); ¹³C NMR (CDCl₃) δ 24.8 (q), 26.8 (t), 27.2 (t), 45.4 (t), 63.3 (d), 160.7 (s), 173.9 (s); HRMS (ESI) calcd for C₇H₁₁N₂O₂ (M + H⁺) 155.0821; found 155.0817.

4.4. Typical procedure for the reductive coupling of **1a** with **2a** (*Table 1, run 2*)

To a solution of **1a** (128 mg, 1 mmol), **2a** (384 mg, 2 mmol), and zinc powder (0.26 g, 4 mmol) in THF (10 mL) was added TiCl₄ (0.22 mL, 2 mmol) dropwise at 5 °C and then the dark blue suspension was stirred for 2 h at this temperature. To the mixture was added 1 M HCl (20 mL) at 5 °C and the mixture was stirred for 15 min at 25 °C. The clear solution was extracted with ethyl acetate three times. The organic layer was washed with aqueous NaCl and dried over MgSO₄. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel to give *dl*-3a, *meso*-3a, and 4a.

4.4.1. (4*R**,4'*R**)-5,5'-Bis(diphenylmethylene)-1,1',3,3'-tetramethyl-[4,4'-biimidazolidine]-2,2'-dione (**dl-3a**)

White solid; *R*f 0.4 (hexanes-ethyl acetate, 1:1); mp 206–207 °C; IR (ATR) 1732, 1713, 1647, 1636 cm⁻¹; ¹H NMR (CDCl₃) δ 2.53 (brs, 6H), 3.23 (brs, 6H), 4.51 (brs, 2H), 6.71–7.45 (m, 20H); ¹³C NMR (CDCl₃) δ 32.3 (q), 60.9 (brd), 114.1 (brs), 126.6 (brd), 127.6 (brd), 128.7 (brd), 129.2 (brd), 130.3 (brs), 134.2 (s), 140.4 (brs), 140.9 (brs), 159.8 (brs). Anal. Calcd for C₃₆H₃₄N₄O₂: C, 77.95; H, 6.18; N, 10.10. Found: C, 78.01; H, 6.20; N, 10.05.

4.4.2. $(4R^*,4'S^*)$ -5,5'-Bis(diphenylmethylene)-1,1',3,3'-tetramethyl-[4,4'-biimidazolidine]-2,2'-dione (**meso-3a**)

White solid; *Rf* 0.25 (hexanes-ethyl acetate, 1:1); mp 226–227 °C; IR (ATR) 1717, 1643, 1624 cm⁻¹; ¹H NMR (CDCl₃) δ 2.33 (brs, 6H), 2.51 (brs, 6H), 4.67 (brs, 2H), 6.69–6.95 (m, 4H), 7.10–7.22 (m, 10H), 7.30–7.42 (m, 6H); ¹³C NMR (CDCl₃) δ 29.2 (brq), 31.7 (q), 62.2 (brd), 115.7 (brs), 126.7 (d), 127.1 (d), 127.4 (brd), 128.9 (d), 130.4 (brd), 134.1 (s), 140.6 (brs), 142.3 (brs), 158.7 (s). Anal. Calcd for C₃₆H₃₄N₄O₂: C, 77.95; H, 6.18; N, 10.10. Found: C, 77.98; H, 6.22; N, 10.04.

4.4.3. (4*R**,4'*R**)-5,5'-Bis(bis(4-fluorophenyl)methylene)-1,1',3,3'tetramethyl-[4,4'-biimidazolidine]-2,2'-dione (**dl-3b**)

White solid; *Rf* 0.7 (hexanes-ethyl acetate, 1:5); mp 215–216 °C; IR (ATR) 1721, 1655, 1628, 1599 cm⁻¹; ¹H NMR (CDCl₃) δ 2.54 (brs, 6H), 3.20 (brs, 6H), 4.40 (brs, 2H), 6.75–7.14 (m, 16H); ¹³C NMR (CDCl₃) δ 32.3 (q), 61.3 (brd), 106.9 (d), 109.8 (brd), 111.2 (brd), 125.6 (brd), 130.1 (s), 131.4 (s), 154.6 (s), 155.5 (s), 157.5 (s). Anal. Calcd for C₃₆H₃₀F₄N₄O₂: C, 69.00; H, 4.83; N, 8.94. Found: C, 68.94; H, 4.85; N, 8.89.

4.4.4. (4*R**,4'S*)-5,5'-Bis(bis(4-fluorophenyl)methylene)-1,1',3,3'tetramethyl-[4,4'-biimidazolidine]-2,2'-dione (**meso-3b**)

Yellow paste; *Rf* 0.35 (hexanes-ethyl acetate, 1:5); ¹H NMR (CDCl₃) δ 2.35 (s, 6H), 2.54 (brs, 6H), 4.63 (brs, 2H), 6.63–7.22 (m, 16H); ¹³C NMR (CDCl₃) δ 29.5 (brq), 31.8 (q), 62.0 (brd), 114.6 (brd), 115.9 (d, *J*_{CCF} = 21.0 Hz), 131.8 (brd), 134.6 (s), 136.1 (brs), 138.0 (brs), 158.4 (s), 161.6 (s, *J*_{CF} = 247.4 Hz), 161.8 (s, *J*_{CF} = 247.4 Hz); HRMS (ESI) calcd for C₃₆H₃₁F₂N₂O₂ (M + H⁺) 627.2383; found 627.2377.

4.4.5. (4R*,4'R*)-5,5'-Bis(bis(4-methoxyphenyl)methylene)-

1,1',3,3'-tetramethyl-[4,4'-biimidazolidine]-2,2'-dione (**dl-3c**)

Yellow paste; *Rf* 0.5 (hexanes-ethyl acetate, 1:2); IR (ATR) 1717, 1655, 1605 cm⁻¹; ¹H NMR (CDCl₃) δ 2.54 (s, 6H), 3.20 (brs, 6H), 3.76 (brs, 6H), 3.86 (brs, 6H), 4.53 (brs, 2H), 6.56–7.13 (m, 16H); ¹³C NMR (CDCl₃) δ 32.2 (q), 54.9 (q), 55.0 (q), 61.2 (d), 113.1 (brd), 113.4 (brd), 114.4 (brd), 129.8 (brd), 130.5 (brd), 131.3 (brd), 133.1 (brs), 133.5 (brs), 133.8 (brs), 157.9 (s), 158.0 (s), 160.1 (brs); HRMS (ESI) calcd for C₄₀H₄₃N₄O₆ (M + H⁺) 675.3183; found 675.3175.

4.4.6. (4R*,4'S*)-5,5'-Bis(bis(4-methoxyphenyl)methylene)-1.1',3.3'-tetramethyl-[4,4'-biimidazolidine]-2,2'-dione (**meso-3c**)

White solid; *Rf* 0.25 (hexanes-ethyl acetate, 1:2); mp 201–203 °C; IR (ATR) 1713, 1636, 1603 cm⁻¹; ¹H NMR (CDCl₃) δ 2.36 (s, 6H), 2.55 (brs, 6H), 3.75 (s, 6H), 3.83 (s, 6H), 4.67 (brs, 2H), 6.63–6.94 (m, 12H), 7.07–7.13 (m, 4H); ¹³C NMR (CDCl₃) δ 29.0 (q), 31.7 (q), 55.0 (q), 55.2 (q), 62.2 (d), 112.8 (d), 113.6 (d), 114.2 (d), 129.8 (d), 131.4 (d), 132.6 (s), 133.5 (s), 134.9 (s), 158.2 (s), 158.6 (s), 158.8 (s). Anal. Calcd for C₄₀H₄₂N₄O₆: C, 71.20; H, 6.27; N, 8.30. Found: C, 71.27; H, 6.30; N, 8.18.

4.4.7. 4-Benzhydryl-1,3-dimethyl-1,3-dihydro-2H-imidazol-2-one (**4a**)

White solid; *Rf* 0.2 (ethyl acetate); mp 149–150 °C; IR (ATR) 1674 cm⁻¹; ¹H NMR (CDCl₃) δ 2.96 (s, 3H), 3.19 (s, 3H), 5.12 (s, 1H), 5.40 (s, 1H), 7.13–7.17 (m, 4H), 7.23–7.28 (m, 2H), 7.29–7.33 (m, 4H); ¹³C NMR (CDCl₃) δ 27.7 (q), 30.0 (q), 47.8 (d), 110.6 (d), 125.0 (s), 126.9 (d), 128.4 (d), 128.5 (d), 140.0 (s), 153.8 (s). Anal. Calcd for C₁₈H₁₈N₂O: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.58; H, 6.54; N, 9.97.

4.4.8. 4-(Bis(4-fluorophenyl)methyl)-1,3-dimethyl-1,3-dihydro-2Himidazol-2-one (**4b**)

Colorless paste; *Rf* 0.55 (ethyl acetate-ethanol, 10:1); IR (ATR) 1620 cm⁻¹; ¹H NMR (CDCl₃) δ 3.07 (s, 3H), 3.34 (s, 3H), 5.15 (s, 1H), 5.53 (s, 1H), 6.99–7.06 (m, 4H), 7.07–7.14 (m, 4H); ¹³C NMR (CDCl₃) δ 28.5 (q), 30.8 (q), 45.8 (d), 111.8 (d), 115.6 (d, *J*_{CCF} = 21.6 Hz), 126.0 (s), 130.1 (d, *J*_{CCCF} = 8.4 Hz), 135.3 (s, *J*_{CCCCF} = 2.4 Hz), 153.3 (s), 161.8 (s, *J*_{CF} = 245.9 Hz); HRMS (ESI) calcd for C₁₈H₁₇F₂N₂O (M + H⁺) 315.1309; found 315.1304.

4.4.9. 4-(Bis(4-methoxyphenyl)methyl)-1,3-dimethyl-1,3-dihydro-2H-imidazol-2-one (**4c**)

Yellow paste; *Rf* 0.3 (ethyl acetate-ethanol, 20:1); IR (ATR) 1674, 1607 cm⁻¹; ¹H NMR (CDCl₃) δ 2.96 (s, 3H), 3.19 (s, 3H), 3.79 (s, 6H), 5.02 (s, 1H), 5.39 (s, 1H), 6.82–6.86 (m, 4H), 7.03–7.06 (m, 4H); ¹³C NMR (CDCl₃) δ 27.8 (q), 30.1 (q), 46.1 (d), 55.0 (q), 110.4 (d), 113.7 (d), 125.7 (s), 129.4 (d), 132.4 (s), 153.8 (s), 158.3 (s); HRMS (ESI) calcd for C₂₀H₂₃N₂O₃ (M + H⁺) 339.1709; found 330.1703.

4.4.10. 4-Benzhydryl-1,3,5-trimethyl-1,3-dihydro-2H-imidazol-2-one (**4h**)

White solid; *Rf* 0.2 (hexanes-ethyl acetate, 1:5); mp 200–201 °C:

IR (ATR) 1632 cm⁻¹; ¹H NMR (CDCl₃) δ 1.44 (s, 3H), 3.12 (s, 3H), 3.35 (s, 3H), 5.40 (s, 1H), 7.06–7.10 (m, 4H), 7.25–7.34 (m, 6H); ¹³C NMR (CDCl₃) δ 8.4 (q), 28.5 (q), 29.0 (q), 46.9 (d), 118.1 (s), 120.7 (s), 127.2 (d), 128.7 (d), 128.9 (d), 139.7 (s), 152.4 (s). Anal. Calcd for C₁₉H₂₀N₂O: C, 78.05; H, 6.90; N, 9.58. Found: C, 78.08; H, 6.91; N, 9.47.

4.4.11. 4-(Bis(4-fluorophenyl)methyl)-1,3,5-trimethyl-1,3-dihydro-2H-imidazol-2-one (**4i**)

Yellow paste; *Rf* 0.25 (ethyl acetate-ethyl alcohol, 20:1); IR (ATR) 1707, 1670, 1643, 1601, 1504 cm⁻¹; ¹H NMR (CDCl₃) δ 1.45 (s, 3H), 2.97 (s, 3H), 3.18 (s, 3H), 5.34 (s, 1H), 6.99–7.07 (m, 8H); ¹³C NMR (CDCl₃) δ 8.4 (q), 27.0 (q), 27.6 (q), 45.5 (q), 115.4 (d, *J*_{CCF} = 21.6 Hz), 116.1 (s), 118.2 (s), 130.2 (d, *J*_{CCCF} = 7.2 Hz), 136.1 (s, *J*_{CCCCF} = 3.6 Hz), 153.1 (s), 161.6 (s, *J*_{CF} = 245.9 Hz); HRMS (ESI) calcd for C₁₉H₁₉F₂N₂O (M + H⁺) 329.1465; found 329.1460.

4.4.12. 4-(Bis(4-methoxyphenyl)methyl)-1,3,5-trimethyl-1,3dihydro-2H-imidazol-2-one (**4j**)

Red paste; *Rf* 0.45 (ethyl acetate-ethyl alcohol, 10:1); IR (ATR) 1670, 1645, 1609, 1508 cm⁻¹; ¹H NMR (CDCl₃) δ 1.46 (s, 3H), 3.02 (s, 3H), 3.22 (s, 3H), 3.81 (s, 6H), 5.28 (s, 1H), 6.83–6.87 (m, 4H), 6.98–7.02 (m, 4H); ¹³C NMR (CDCl₃) δ 8.3 (q), 27.3 (q), 27.9 (q), 45.2 (d), 54.9 (q), 113.6 (s), 116.3 (s), 119.6 (s), 129.6 (d), 132.4 (s), 152.7 (s), 158.2 (s); HRMS (ESI) calcd for C₂₁H₂₅N₂O₃ (M + H⁺) 353.1865; found 353.1862.

4.4.13. 4-Benzhydryl-5-isobutyl-1,3-dimethyl-1,3-dihydro-2Himidazol-2-one (**4***k*)

Yellow paste; *Rf* 0.2 (ethyl acetate); IR (ATR) 1616 cm⁻¹; ¹H NMR (CDCl₃) δ 0.72 (d, 6H, *J* = 6.6 Hz), 1.49–1.58 (m, 1H), 1.85 (d, 2H, *J* = 7.6 Hz), 3.02 (s, 3H), 3.39 (s, 3H), 5.51 (s, 1H), 7.06–7.12 (m, 4H), 7.24–7.34 (m, 6H); ¹³C NMR (CDCl₃) δ 21.8 (q), 28.9 (d), 29.1 (q), 29.6 (q), 31.1 (t), 46.3 (d), 120.9 (s), 122.0 (s), 127.0 (d), 128.5 (d), 128.8 (d), 139.4 (s), 152.4 (s); HRMS (ESI) calcd for C₂₂H₂₇N₂O (M + H⁺) 335.2123; found 335.2118.

4.4.14. 4-Benzhydryl-5-benzyl-1,3-dimethyl-1,3-dihydro-2Himidazol-2-one (**4**I)

Yellow paste; *Rf* 0.25 (hexanes-ethyl acetate, 1:5); IR (ATR) 1711, 1618 cm⁻¹; ¹H NMR (CDCl₃) δ 3.08 (s, 3H), 3.12 (s, 3H), 3.31 (s, 2H), 5.50 (s, 1H), 6.87–6.91 (m, 2H), 7.06–7.11 (m, 4H), 7.12–7.28 (m, 9H); ¹³C NMR (CDCl₃) δ 28.3 (t), 28.6 (q), 29.3 (q), 46.8 (d), 119.9 (s), 122.1 (s), 126.4 (d), 127.1 (d), 127.4 (d), 128.4 (d), 128.6 (d), 128.8 (d), 136.9 (s), 139.4 (s), 152.8 (s); HRMS (ESI) calcd for C₂₅H₂₅N₂O (M + H⁺) 369.1967; found 369.1961.

4.4.15. 4-Benzhydryl-5-isopropyl-1,3-dimethyl-1,3-dihydro-2H-imidazol-2-one (**4m**)

Yellow paste; *Rf* 0.25 (hexanes-ethyl acetate, 1:5); IR (ATR) 1647, 1624 cm⁻¹; ¹H NMR (CDCl₃) δ 1.09 (d, 6H, *J* = 7.3 Hz), 2.61–2.69 (m, 1H), 3.02 (s, 3H), 3.49 (s, 3H), 5.61 (s, 1H), 7.07–7.12 (m, 4H), 7.24–7.34 (m, 6H); ¹³C NMR (CDCl₃) δ 20.7 (q), 23.9 (d), 29.9 (q), 30.4 (q), 46.1 (d), 120.2 (s), 126.9 (s), 127.1 (d), 128.7 (d), 128.8 (d), 139.6 (s), 152.6 (s); HRMS (ESI) calcd for C₂₁H₂₅N₂O (M + H⁺) 321.1967; found 321.1963.

4.4.16. Benzhydryl-2-methyl-2,5,6,7-tetrahydro-3H-pyrrolo[1,2-c] imidazol-3-one (**4n**)

Yellow paste; *Rf* 0.25 (ethyl acetate-ethanol, 10:1); IR (ATR) 1684, 1653 cm⁻¹; ¹H NMR (CDCl₃) δ 1.63 (t, 2H, *J* = 7.5 Hz), 2.07–2.14 (m, 2H), 2.93 (s, 3H), 3.62 (t, 2H, *J* = 7.2 Hz), 5.16 (s, 1H), 7.09–7.15 (m, 4H), 7.23–7.35 (m, 6H); ¹³C NMR (CDCl₃) δ 22.1 (t), 27.4 (t), 27.7 (q), 41.6 (t), 47.6 (d), 115.3 (s), 124.4 (s), 126.8 (d), 128.3 (d), 128.7 (d), 140.5 (s), 150.3 (s); HRMS (ESI) calcd for C₂₀H₂₁N₂O

(M + H⁺) 305.1654; found 305.1650.

4.4.17. 1-(Bis(4-fluorophenyl)methyl)-2-methyl-2,5,6,7-tetrahydro-3H-pyrrolo[1,2-c]imidazol-3-one (**40**)

Yellow paste; *Rf* 0.2 (ethyl acetate-ethyl alcohol, 10:1); IR (ATR) 1647, 1618, 1601, 1504 cm⁻¹; ¹H NMR (CDCl₃) δ 1.68 (t, 2H, *J* = 7.4 Hz), 2.13–2.20 (m, 2H), 3.00 (s, 3H), 3.84–3.90 (m, 2H), 5.15 (s, 1H), 7.00–7.09 (m, 8H); ¹³C NMR (CDCl₃) δ 22.1 (t), 27.2 (t), 28.3 (q), 42.8 (t), 45.7 (d), 115.3 (d, *J*_{CCCF} = 20.7 Hz), 116.2 (s), 125.6 (s), 130.1 (d, *J*_{CCCF} = 8.4 Hz), 135.6 (s, *J*_{CCCCF} = 3.6 Hz), 149.5 (s), 161.6 (s, *J*_{CCF} = 246.8 Hz); HRMS (ESI) calcd for C₂₀H₁₉F₂N₂O (M + H⁺) 341.1465; found 341.1460.

4.4.18. 1-(Bis(4-methoxyphenyl)methyl)-2-methyl-2,5,6,7tetrahydro-3H-pyrrolo[1,2-c]imidazol-3-one (**4p**)

Yellow paste; *Rf* 0.25 (ethyl acetate-ethyl alcohol, 10:1); IR (ATR) 1672, 1647, 1609 cm⁻¹; ¹H NMR (CDCl₃) δ 1.68 (t, 2H, *J* = 7.6 Hz), 2.09–2.16 (m, 2H), 2.96 (s, 3H), 3.72 (t, 2H, *J* = 6.9 Hz), 3.80 (s, 6H), 5.06 (s, 1H), 6.82–6.86 (m, 4H), 6.99–7.03 (m, 4H); ¹³C NMR (CDCl₃) δ 22.1 (t), 27.4 (t), 27.9 (q), 42.1 (t), 45.8 (d), 54.9 (q), 113.6 (d), 116.4 (s), 124.6 (s), 129.5 (d), 132.6 (s), 149.9 (s), 158.2 (s); HRMS (ESI) calcd for C₂₂H₂₅N₂O₃ (M + H⁺) 365.1865; found 365.1861.

4.4.19. 4-(Hydroxydiphenylmethyl)-1,3-dimethyl-1,3-dihydro-2Himidazol-2-one (**5a**)

White solid; *Rf* 0.2 (ethyl acetate); mp 216–218 °C; IR (ATR) 3218, 3152, 1672, 1649 cm⁻¹; ¹H NMR (CDCl₃) δ 2.97 (s, 3H), 3.08 (s, 3H), 4.95 (s, 1H), 5.35 (s, 1H), 7.25–7.34 (m, 6H), 7.36–7.39 (m, 4H); ¹³C NMR (CDCl₃) δ 29.7 (q), 30.4 (q), 76.6 (s), 112.2 (d), 126.9 (d), 127.5 (d), 127.7 (s), 128.0 (d), 143.9 (s), 154.2 (s). Anal. Calcd for C₁₈H₁₈N₂O₂: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.48; H, 6.16; N, 9.48.

4.4.20. 4-(Bis(4-fluorophenyl)(hydroxy)methyl)-1,3-dimethyl-1,3dihydro-2H-imidazol-2-one (**5b**)

White solid; *Rf* 0.55 (ethyl acetate-ethanol, 10:1); mp 249–250 °C; IR (ATR) 3190, 1661, 1601 cm⁻¹; ¹H NMR (CDCl₃) δ 2.96 (s, 3H), 3.09 (s, 3H), 5.21 (s, 1H), 5.35 (s, 1H), 6.98–7.05 (m, 4H), 7.30–7.37 (m, 4H); ¹³C NMR (CDCl₃) δ 29.2 (q), 29.9 (q), 75.3 (s), 111.6 (d), 114.3 (d, *J*_{CCF} = 21.6 Hz), 126.9 (s), 128.4 (d, *J*_{CCCF} = 8.4 Hz), 139.7 (s, *J*_{CCCCF} = 2.4 Hz), 153.8 (s), 161.5 (s, *J*_{CF} = 246.2 Hz). Anal. Calcd for C₁₈H₁₆F₂N₂O₂: C, 65.45; H, 4.88; N, 8.48. Found: C, 65.40; H, 4.93; N, 8.43.

4.4.21. 4-(9-Hydroxy-9,10-dihydroanthracen-9-yl)-1,3-dimethyl-1,3-dihydro-2H-imidazol-2-one (5d)

White solid; *Rf* 0.4 (ethyl acetate-ethanol, 20:1); mp 235–236 °C; IR (ATR) 3231, 1663 cm⁻¹; ¹H NMR (CDCl₃) δ 2.86 (s, 3H), 3.09 (s, 3H), 3.86 (s, 1H), 3.95 (d, 1H, *J* = 18.4 Hz), 4.02 (d, 1H, *J* = 8.4 Hz), 5.69 (s, 1H), 7.27–7.34 (m, 6H), 7.68–7.72 (m, 2H); ¹³C NMR (CDCl₃) δ 28.8 (q), 29.9 (q), 35.0 (t), 71.5 (s), 109.8 (d), 124.5 (s), 125.8 (d), 126.0 (d), 127.1 (d), 127.3 (d), 135.6 (s), 139.5 (s), 153.5 (s). Anal. Calcd for C₁₉H₁₈N₂O₂: C, 74.49; H, 5.92; N, 9.14. Found: C, 74.47; H, 5.92; N, 9.09.

4.4.22. 4-(5-Hydroxy-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5yl)-1,3-dimethyl-1,3-dihydro-2H-imidazol-2-one (**5e**)

White solid; *Rf* 0.15 (ethyl acetate); mp 261–262 °C; IR (ATR) 3159, 1670 cm⁻¹; ¹H NMR (CDCl₃) δ 2.73 (s, 3H), 2.76–2.85 (m, 2H), 3.08 (s, 3H), 3.15–3.24 (m, 2H), 4.52 (brs, 1H), 5.44 (s, 1H), 7.05–7.09 (m, 2H), 7.17–7.25 (m, 4H), 7.97–8.01 (m, 2H); ¹³C NMR (CDCl₃) δ 28.8 (q), 30.5 (q), 32.1 (t), 72.3 (s), 111.0 (d), 125.6 (d), 126.0 (d), 127.7 (d), 127.8 (s), 130.2 (d), 137.1 (s), 141.6 (s), 153.5 (s). Anal. Calcd for C₂₀H₂₀N₂O₂: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.95; H, 6.30; N, 8.68.

4.4.23. 4-(5-Hydroxy-5H-dibenzo[a,d][7]annulen-5-yl)-1,3dimethyl-1,3-dihydro-2H-imidazol-2-one (5f)

Colorless paste; *Rf* 0.4 (ethyl acetate-ethanol, 20:1); IR (ATR) 1699, 1653, 1647, 1636, 1616 cm⁻¹; ¹H NMR (CDCl₃) δ 2.61 (s, 3H), 3.20 (s, 3H), 3.33 (brs, 1H), 5.45 (s, 1H), 6.84 (s, 2H), 7.30–7.34 (m, 4H), 7.43–7.48 (m, 2H), 8.05–8.09 (m, 2H); ¹³C NMR (CDCl₃) δ 28.9 (q), 30.9 (q), 72.4 (s), 112.3 (d), 124.2 (s), 124.5 (d), 126.9 (d), 128.3 (d), 128.6 (d), 130.6 (d), 132.6 (s), 138.9 (s), 152.7 (s); HRMS (ESI) calcd for C₂₀H₁₉N₂O₂ (M + H⁺) 319.1447; found 319.1442.

4.4.24. 4-(9-Hydroxy-9H-xanthen-9-yl)-1,3-dimethyl-1,3-dihydro-2H-imidazol-2-one (**5g**)

Yellow paste; *Rf* 0.25 (ethyl acetate-EtOH, 5:1); IR (ATR) 1663, 1601 cm⁻¹; ¹H NMR (CDCl₃) δ 1.88 (brs, 1H), 2.18 (s, 3H), 3.30 (s, 3H), 6.32 (s, 1H), 6.90–6.97 (m, 4H), 7.03–7.07 (m, 2H), 7.32–7.37 (m, 2H); ¹³C NMR (CDCl₃) δ 28.2 (q), 30.4 (q), 77.7 (s), 110.2 (d), 116.5 (d), 118.1 (s), 121.7 (s), 122.9 (d), 129.4 (d), 130.2 (d), 151.1 (s), 153.6 (s); HRMS (ESI) calcd for C₁₈H₁₇N₂O₃ (M + H⁺) 309.1239; found 309.1234.

4.4.25. 4,5-Dibenzhydryl-1,3-dimethyl-1,3-dihydro-2H-imidazol-2-one (**6a**)

White solid; *Rf* 0.5 (hexanes-ethyl acetate, 1:5); mp 219–220 °C; IR (ATR) 1668, 1622, 1597 cm⁻¹; ¹H NMR (CDCl₃) δ 2.86 (s, 6H), 5.23 (s, 2H), 6.95–7.00 (m, 8H), 7.17–7.25 (m, 12H); ¹³C NMR (CDCl₃) δ 29.2 (q), 45.8 (d), 121.0 (s), 126.8 (d), 128.4 (d), 128.9 (d), 140.2 (s), 153.7 (s). Anal. Calcd for C₃₁H₂₈N₂O: C, 83.75; H, 6.35; N, 6.30. Found: C, 83.79; H, 6.33; N, 6.23.

4.4.26. 4,5-Bis(bis(4-fluorophenyl)methyl)-1,3-dimethyl-1,3-dihydro-2H-imidazol-2-one (**6b**)

Pale yellow paste; *Rf* 0.5 (hexanes-ethyl acetate, 1:2); IR (ATR) 1711, 1678, 1601 cm⁻¹; ¹H NMR (CDCl₃) δ 2.86 (s, 6H), 5.15 (s, 2H), 6.88–6.97 (m, 8H); ¹³C NMR (CDCl₃) δ 29.1 (q), 44.5 (d), 115.5 (d, *J*_{CCCF} = 21.0 Hz), 120.6 (s), 130.2 (d, *J*_{CCCF} = 7.8 Hz), 135.6 (s, *J*_{CCCCF} = 2.7 Hz), 153.6 (s), 161.7 (s, *J*_{CF} = 246.8 Hz); HRMS (ESI) calcd for C₃₁H₂₅F₄N₂O (M + H⁺) 517.1903; found 517.1897.

4.4.27. 4,5-Bis(bis(4-methoxyphenyl)methyl)-1,3-dimethyl-1,3-dihydro-2H-imidazol-2-one (**6***c*)

Yellow paste; *Rf* 0.55 (ethyl acetate-ethanol, 20:1); IR (ATR) 1686, 1609 cm⁻¹; ¹H NMR (CDCl₃) δ 2.86 (s, 6H), 3.78 (s, 12H), 5.14 (s, 2H), 6.73–6.77 (m, 8H), 6.87–6.91 (m, 8H); ¹³C NMR (CDCl₃) δ 29.0 (q), 44.0 (d), 55.0 (q), 113.5 (d), 120.9 (s), 129.7 (d), 132.5 (s), 153.5 (s), 158.1 (s); HRMS (ESI) calcd for C₃₅H₃₇N₂O₅ (M + H⁺) 565.2702; found 565.2697.

4.4.28. 1,3-Dimethyl-4-(1,1,2,2-tetraphenylethyl)-1,3-dihydro-2Himidazol-2-one (**7a**)

Colorless paste; *Rf* 03 (hexanes-ethyl acetate, 1:2); IR (ATR) 1678 cm⁻¹; ¹H NMR (CDCl₃) δ 2.29 (s, 3H), 3.15 (s, 3H), 5.20 (s, 1H), 5.91 (s, 1H), 6.59–6.64 (m, 4H), 7.00–7.06 (m, 4H), 7.07–7.12 (m, 2H), 7.20–7.36 (m, 11H); ¹³C NMR (CDCl₃) δ 30.1 (q), 30.4 (q), 57.1 (s), 62.4 (d), 112.6 (d), 126.4 (d), 127.4 (d), 127.5 (d), 127.7 (d), 128.4 (s), 130.9 (d), 131.0 (d), 140.0 (s), 141.4 (s), 153.6 (s); HRMS (ESI) calcd for C₃₁H₂₉N₂O (M + H⁺) 445.2280; found 445.2275.

4.4.29. 1,3-Dimethyl-4-(1,1,2,2-tetrakis(4-fluorophenyl)ethyl)-1,3dihydro-2H-imidazol-2-one (**7b**)

Pale yellow paste; *Rf* 0.35 (hexanes-ethyl acetate, 1.2); IR (ATR) 1713, 1684, 1601 cm⁻¹; ¹H NMR (CDCl₃) δ 2.31 (s, 3H), 3.16 (s, 3H), 5.11 (s, 1H), 5.85 (s, 1H), 6.52–6.57 (m, 4H), 6.75–6.81 (m, 4H), 7.00–7.06 (m, 4H), 7.14–7.20 (m, 4H); ¹³C NMR (CDCl₃) δ 30.1 (q), 30.4 (q), 56.0 (s), 60.7 (d), 112.6 (d), 114.7 (d, *J*_{CCF} = 20.4 Hz), 114.9 (d, *J*_{CCF} = 21.0 Hz), 127.5 (s), 132.0 (d, *J*_{CCCF} = 7.8 Hz), 132.4 (d,

 $J_{CCCF} = 8.4$ Hz), 135.2 (s, $J_{CCCCF} = 3.0$ Hz), 136.6 (s, $J_{CCCCF} = 3.0$ Hz), 153.5 (s), 161.5 (s, $J_{CF} = 247.7$ Hz), 161.9 (s, $J_{CF} = 249.5$ Hz); HRMS (ESI) calcd for $C_{31}H_{25}F_4N_2O$ (M + H⁺) 517.1903; found 517.1898.

4.4.30. 1,3-Dimethyl-4-(1,1,2,2-tetrakis(4-methoxyphenyl)ethyl)-1,3-dihydro-2H-imidazol-2-one (7c)

Yellow paste; *R*f 0.3 (ethyl acetate); IR (ATR) 1670, 1605 cm⁻¹; ¹H NMR (CDCl₃) δ 2.32 (s, 3H), 3.15 (s, 3H), 3.72 (s, 6H), 3.84 (s, 6H), 5.02 (s, 1H), 5.89 (s, 1H), 6.50–6.54 (m, 4H), 6.57–6.61 (m, 4H), 6.79–6.83 (m, 4H), 7.08–7.13 (m, 4H); ¹³C NMR (CDCl₃) δ 29.9 (q), 30.2 (q), 54.8 (q), 55.0 (q), 55.7 (s), 60.6 (d), 112.1 (d), 112.7 (d), 128.6 (s), 131.5 (d), 131.9 (d), 132.3 (s), 133.8 (s), 153.5 (s), 157.7 (s), 158.3 (s); HRMS (ESI) calcd for C₃₅H₃₇N₂O₅ (M + H⁺) 565.2702; found 565.2695.

4.4.31. 4-Benzhydryl-5-methyl-1,3-dihydro-2H-imidazol-2-one (10b)

Yellow solid; *Rf* 0.15 (ethyl acetate); mp 225–226 °C; IR (ATR) 3171 (br), 1686, 1670 cm⁻¹; ¹H NMR (CDCl₃) δ 1.78 (s, 3H), 5.23 (s, 1H), 7.11–7.15 (m, 4H), 7.20–7.31 (m, 6H), 7.77 (brs, 1H), 9.90 (brs, 1H); ¹³C NMR (CDCl₃) δ 9.2 (q), 46.7 (d), 115.0 (s), 117.9 (s), 126.6 (d), 128.4 (d), 128.6 (d), 141.3 (s), 155.1 (s). Anal. Calcd for C₁₇H₁₆N₂O: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.18; H, 6.14; N, 10.53.

4.4.32. 4-Benzhydryl-5-isobutyl-1,3-dihydro-2H-imidazol-2-one (**10c**)

White solid; *Rf* 0.5 (ethyl acetate); mp 227–229 °C; IR (ATR) 3156 (br), 1686, 1647 cm⁻¹; ¹H NMR (CDCl₃) δ 0.84 (d, 3H *J* = 6.6 Hz), 1.73–1.83 (m, 1H), 2.13 (d, 2H *J* = 7.5 Hz), 5.27 (s, 1H), 7.11–7.15 (m, 5H), 7.21–7.26 (m, 2H), 7.27–7.32 (m, 4H), 9.58 (brs, 1H); ¹³C NMR (CDCl₃-DMSO-d₆) δ 21.4 (q), 27.1 (d), 32.2 (t), 45.8 (d), 117.6 (s), 117.9 (s), 125.8 (d), 127.5 (d), 127.9 (d), 141.1 (s), 154.4 (s). Anal. Calcd for C₂₀H₂₂N₂O: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.46; H, 9.17; N, 9.06.

4.4.33. 4-Benzhydryl-5-benzyl-1,3-dihydro-2H-imidazol-2-one (10d)

Pale yellow paste; *Rf* 0.5 (ethyl acetate); IR (ATR) 3202 (br), 1713, 1617 cm⁻¹; ¹H NMR (CDCl₃) δ 3.51 (s, 2H), 5.28 (s, 1H), 7.02–7.06 (m, 2H), 7.10–7.31 (m, 13H), 7.78 (brs, 1H), 9.07 (brs, 1H); ¹³C NMR (CDCl₃) δ 30.2 (t), 46.5 (d), 118.0 (s), 118.8 (s), 126.3 (d), 126.7 (d), 128.3 (d), 128.36 (d), 128.44 (d), 128.6 (d), 138.0 (s), 141.2 (s), 155.0 (s); HRMS (ESI) calcd for C₂₃H₂₁N₂O (M + H⁺) 341.1654; found 341.1650.

4.4.34. 1-Benzhydryl-2,5,6,7-tetrahydro-3H-pyrrolo[1,2-c] imidazol-3-one (**10f**)

Yellow paste; *Rf* 0.15 (ethyl acetate); IR (ATR) 3215 (br), 1705, 1655 cm⁻¹; ¹H NMR (CDCl₃) δ 1.80–1.85 (m, 2H), 2.14–2.21 (m, 2H), 3.56 (t, 2H, *J* = 7.0 Hz), 5.12 (s, 1H), 7.15–7.19 (m, 4H), 7.22–7.26 (m, 2H), 7.27–7.32 (m, 2H), 7.53 (brs, 1H); ¹³C NMR (CDCl₃) δ 22.0 (t), 27.9 (t), 41.2 (t), 48.1 (d), 113.8 (s), 125.3 (s), 126.7 (d), 128.2 (d), 128.8 (d), 141.1 (s), 150.8 (s); HRMS (ESI) calcd for C₁₉H₁₉N₂O (M + H⁺) 291.1497; found 291.1496.

4.5. Typical procedure for the reduction of **5e-g** to **4e-g** (Scheme 3)

To a solution of **5e** (128 mg, 0.3 mmol) and zinc powder (78 mg, 1.2 mmol) in THF (5 mL) was added TiCl₄ (0.066 mL, 0.6 mmol) dropwise at 25 °C and then the suspension was refluxed for 18 h. To the mixture was added 1 M HCl (10 mL) at 25 °C and the mixture was stirred for 15 min at 25 °C. The clear solution was extracted with ethyl acetate three times. The organic layer was washed with aqueous NaCl and dried over MgSO₄. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on

silica gel to give **4e**.

4.5.1. 4-(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)-1,3dimethyl-1,3-dihydro-2H-imidazol-2-one (**4e**)

White solid; *Rf* 0.25 (ethyl acetate); mp 225–227 °C; IR (ATR) 1653, 1624 cm⁻¹; ¹H NMR (CDCl₃) δ 2.73–2.82 (m, 2H), 2.93 (s, 3H), 3.30 (s, 3H), 3.33–3.41 (m, 2H), 4.89 (d, 1H, *J* = 1.7 Hz), 5.40 (d, 1H, *J* = 1.7 Hz), 7.11–7.18 (m, 4H), 7.19–7.23 (m, 2H), 7.24–7.27 (m, 2H); ¹³C NMR (CDCl₃) δ 28.6 (q), 30.1 (q), 31.5 (t), 51.1 (d), 110.2 (d), 125.0 (s), 126.0 (d), 127.6 (d), 130.6 (d), 130.7 (d), 136.7 (s), 139.8 (s), 153.8 (s). Anal. Calcd for C₂₀H₂₀N₂O: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.96; H, 6.63; N, 9.13.

4.5.2. 4-(5H-Dibenzo[a,d][7]annulen-5-yl)-1,3-dimethyl-1,3dihydro-2H-imidazol-2-one (**4f**)

Pale yellow paste; *Rf* 0.3 (ethyl acetate-ethanol, 20:1); IR (ATR) 1653, 1618 cm⁻¹; ¹H NMR (CDCl₃) δ 2.79 (s, 3H), 3.12 (s, 3H), 5.17 (brs, 1H), 5.23 (brs, 1H), 6.86 (s, 2H), 7.29–7.33 (m, 2H), 7.34–7.40 (m, 4H), 7.43–7.45 (m, 2H); ¹³C NMR (CDCl₃) δ 28.9 (q), 30.7 (q), 50.5 (d), 110.9 (d), 120.3 (s), 127.3 (d), 128.8 (d), 129.9 (d), 130.3 (d), 134.5 (s), 136.0 (s), 153.2 (s); HRMS (ESI) calcd for C₂₀H₁₉N₂O (M + H⁺) 303.1497; found 303.1494.

4.5.3. 1,3-Dimethyl-4-(9H-xanthen-9-yl)-1,3-dihydro-2H-imidazol-2-one (**4g**)

Colorless paste; *Rf* 0.25 (ethyl acetate); IR (ATR) 1618 cm⁻¹; ¹H NMR (CDCl₃) δ 2.75 (s, 3H), 3.46 (s, 3H), 5.26 (s, 1H), 6.40 (s, 1H), 7.00–7.06 (m, 4H), 7.08–7.12 (m, 2H), 7.24–7.29 (m, 2H); ¹³C NMR (CDCl₃) δ 29.1 (q), 31.5 (q), 34.9 (d), 111.8 (d), 116.7 (d), 119.2 (s), 123.6 (d), 124.5 (s), 128.5 (d), 128.9 (d), 150.9 (s), 153.5 (s); HRMS (ESI) calcd for C₁₈H₁₇N₂O₂ (M + H⁺) 293.1290; found 293.1285.

4.5.4. 4-(Anthracen-9-yl)-1,3-dimethyl-1,3-dihydro-2H-imidazol-2-one (**8**)

Yellow solid; *Rf* 0.35 (ethyl acetate-ethanol, 20:1); mp 222–223 °C; IR (ATR) 1680 cm⁻¹; ¹H NMR (CDCl₃) δ 2.86 (s, 3H), 3.49 (s, 3H), 6.39 (s, 1H), 7.47–7.53 (m, 4H), 7.87–7.92 (m, 2H), 8.03–8.09 (m, 2H), 8.57 (s, 1H); ¹³C NMR (CDCl₃) δ 28.1 (q), 30.5 (q), 111.6 (d), 118.9 (s), 122.5 (s), 125.4 (d), 125.5 (d), 126.6 (d), 128.5 (d), 128.8 (d), 131.1 (s), 132.1 (s), 153.8 (s). Anal. Calcd for C₁₉H₁₆N₂O: C, 79.14; H, 5.59; N, 9.72. Found: C, 79.10; H, 5.61; N, 9.66.

4.6. X-ray crystallographic analysis

All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo K α radiation. The structure was solved by direct methods with SIR-97 and refined

with SHELXL-97. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed using the YADOKARI-XG software package. Crystal data of **dl-3a**, **meso-3a**, **dl-3b**, **meso-3c**, **5b**, **5d**, **5e**, **6a**, and **8** are as follows: CCDC 1583196–1583204 contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.ac. uk/data/cif.

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