Tandem Reactions of 2-Methylimidazoline and 1,2-Dimethylimidazoline with Various Benzoyl Chlorides

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Abstract: The reactions of 2-methylimidazoline with excess benzoyl chlorides under mild conditions generated *N*,*N*′-diacyl-β-keto cyclic ketene-*N*,*N*′-acetals. Conversely, the corresponding reactions of 1,2-dimethylimidazoline under the same conditions stereoselectively formed the ring-opened (*Z*)-vinyl benzoates. The latter reactions feature the formation of carbon–carbon bonds, carbon–nitrogen bonds, and carbon–oxygen bonds in one sequential cascade.

Key words: acyl ketene-*N*,*N*′-acetal, carbon–carbon bond formation, 2-methylimidazoline, 1,2-dimethylimidazoline

Carbon–carbon bond construction is fundamental to organic synthesis. Enamines are important substrates for C–C bond forming reactions based on their β-carbon nucleophilicities. Ketene-*N*,*N*′-acetals, also known as 1,1-enediamines (Figure 1), with two electron-donating nitrogens connected to one end of a double bond, are of particular interest due to their enhanced nucleophilicities. The acyclic ketene-*N*,*N*′-acetals **1**, where both R^1 and R^2 are alkyl groups, were first synthesized by McElvain and Tate in the 1940s.[1] Later, substantial research efforts were expended to develop preparative methods for the ketene-*N*,*N*′-acetals[2–6] and to explore their reactions with various electrophiles,[7–13] dienes[14–18] and dipolar reagents.[19–22] Compared to the dialkyl ketene-*N*,*N*′-acetals **1**, much less attention has been paid to the acyl ketene-*N*,*N*′-acetals **2** and **3**, where one or both alkyl groups are replaced by an acyl group.

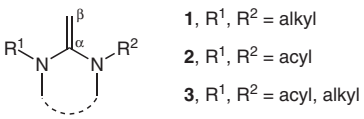
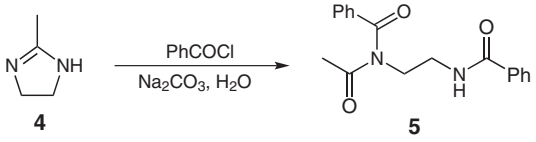


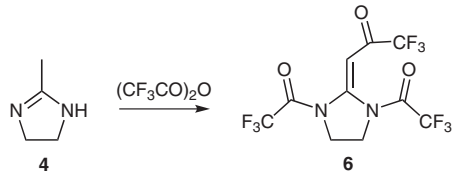
Figure 1 Structure of ketene-*N*,*N*′-acetals

2-Methylimidazoline **4**, which is a precursor of cyclic ketene-*N*,*N*′-acetals,[2] was reported to react with two equivalents of benzoyl chloride in aqueous carbonate to give ring-opened product **5** (Scheme 1).[23a] In this reaction, two nitrogens were benzoylated; no C–C bond was formed. An extremely strong electrophile, trifluoroacetic anhydride, was reported to react with 2-methylimidazoline, forming ring-retained triacylated products (Scheme 2).[23b] This was the first and, so far, the only example that showed the nucleophilicity of a diacyl cyclic ketene-*N*,*N*′-acetal. Recently, 2-methylthiazolines **7**, which are analogues of **4**, were reported to react with acid chlorides in triethylamine/acetonitrile to give ring-retained product **8** in good yields;[24–26] in this case, one C–C bond formed at the β-carbon (Scheme 3). The *N*-acyl cyclic ketene-*N*,*S*-acetal intermediates **7′** acted as carbon nucleophiles, reacting with more acid chloride in these reactions.

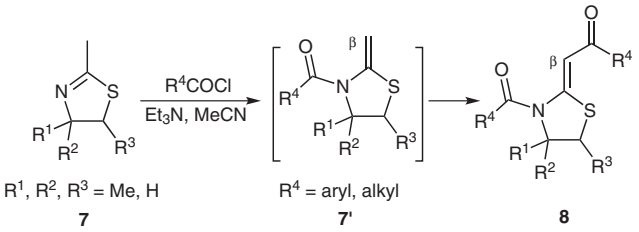
We speculated that 2-methylimidazoline **4** may also react with various acid chlorides to generate acyl cyclic ketene acetal intermediates that could then further react, forming ring-retained products under appropriate conditions. In-



Scheme 1 Reaction of 2-methylimidazoline with benzoyl chloride in aqueous carbonate



Scheme 2 Reaction of 2-methylimidazoline with trifluoroacetic anhydride



Scheme 3 Reaction of 2-methylthiazolines with acid chlorides

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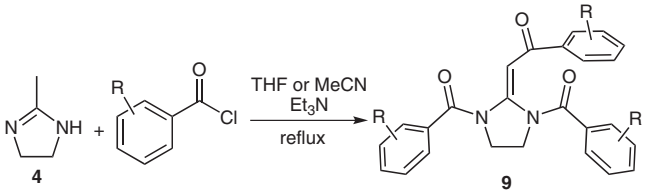
deed, tricyclic 1,8-naphthyridinetetraones were conveniently synthesized recently in our lab via tandem reactions of **4** with diacid chlorides.[27] Herein, we report the reactions of **4** with various substituted benzoyl chlorides in refluxing triethylamine in either tetrahydrofuran or acetonitrile. Ring-retained triacylated products **9** were obtained in moderate to good yields. Two C–N bonds and one C–C bond were formed in each reaction (Table 1). Acetonitrile appeared to be a superior solvent to tetrahydrofuran due to its larger polarity and higher boiling point (bp: 82 °C vs. 69 °C). Better yields were obtained for **9a** and **9c** in acetonitrile than in tetrahydrofuran after refluxing for three hours (entries 1, 2, 4 and 6). Prolonged refluxing (16 h) in tetrahydrofuran enhanced the yield of **9c** (entries 4 and 5) but this was still lower than using acetonitrile for only three hours (entries 5 and 6).

The electronic nature of the R group has no apparent impact on the product yield under these conditions (Table 1, entries 6–16). When the R group increases the electrophilicity of a benzoyl chloride, it simultaneously decreases the nucleophilicity of the diacyl ketene-*N*,*N*′-acetal intermediate, and vice versa. Thus, the substituent effect was largely cancelled out because the same substituent appears in both nucleophile (diacyl ketene-*N*,*N*′-acetal) and electrophile (benzoyl chloride). These tandem reactions clearly demonstrate the pronounced nucleophilicity of the diacyl ketene-*N*,*N*′-acetal **2**. These results are of special interest because 2-alkyl imidazoline derivatives constitute an important class of biologically active compounds.[28]

The mechanism shown in Scheme 4 accounts for the formation of **9a**. The first acylation takes place on the sp^2 nitrogen to generate zwitterion intermediate **4a**, followed by loss of HCl to give $Et_3NH^+ Cl^-$ and mono-acylated product **4c**. The second N-acylation occurs on the second nitrogen followed by proton removal from the β-carbon to give the *N*,*N*′-diacyl ketene acetal **4f**. Both nitrogens in **4f** activate the double bond to initiate nucleophilic attack by the β-carbon on a third equivalent of acid chloride, despite the fact that both nitrogens are benzoylated. After chloride loss and proton abstraction from **4h**, tribenzoylated **9a** is produced. At this point, the β-carbons in **9a–c** were deactivated enough to prevent further reaction with benzoyl chloride (Scheme 5).

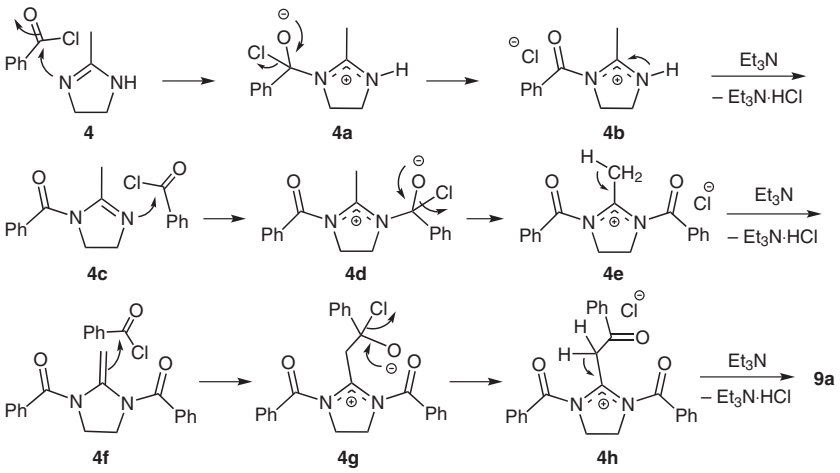
Table 1 Reactions of 2-Methylimidazoline **4** with Various Benzoyl Chlorides[a]



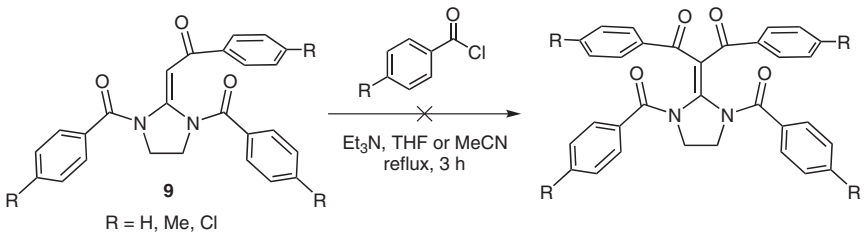
4 **9**

Entry	R	Solvent	Time (h)	Product	Yield (%)[b]
1	H	THF	3	**9a**	71
2	H	MeCN	3	**9a**	80
3	4-Cl	THF	3	**9b**	65
4	4-Me	THF	3	**9c**	58
5	4-Me	THF	16	**9c**	67
6	4-Me	MeCN	3	**9c**	78
7	4-MeO	MeCN	6	**9d**	73
8	4-F	MeCN	6	**9e**	75
9	3-Cl	MeCN	6	**9f**	76
10	3-Me	MeCN	6	**9g**	72
11	3-MeO	MeCN	6	**9h**	75
12	3-F	MeCN	6	**9i**	76
13	3-Br	MeCN	6	**9j**	78
14	2-Cl	MeCN	6	**9k**	69
15	2-F	MeCN	6	**9l**	68
16	2-Br	MeCN	6	**9m**	70

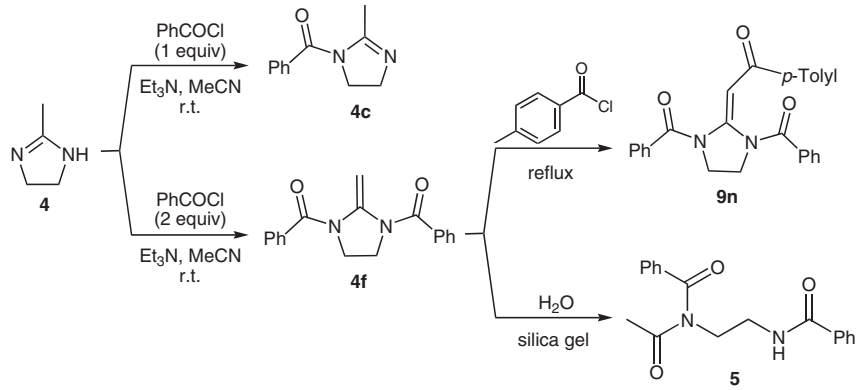
[a] The ratio of **4**/acid chloride/Et_3N = 1:3.5:4.
[b] Isolated yield after column chromatography.



Scheme 4 Proposed mechanism for the formation of **9a**



Scheme 5 Unsuccessful tetrabenzoylation



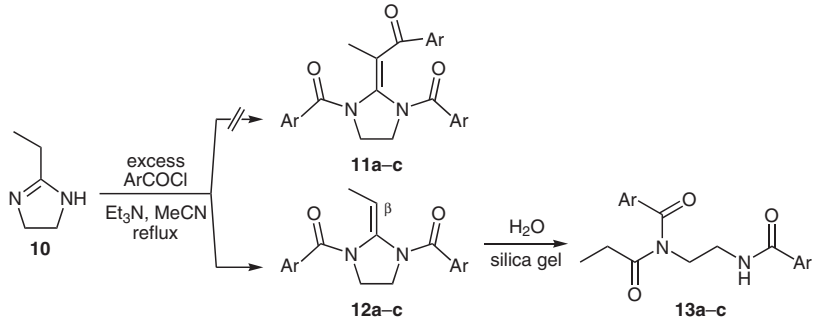
Scheme 6 Experimental support for the proposed mechanism

The proposed mechanism (Scheme 4) was supported by the following experiments: 2-methylimidazoline reacted with one equivalent of benzoyl chloride (Scheme 6) affording mono-N-benzoylated product **4c**; two equivalents of benzoyl chloride gave dibenzoyl ketene acetal **4f**. The latter was moisture-sensitive and hydrolyzed to ring-opened product **5** during silica-gel column chromatography. Moreover, ketene acetal **4f** generated in-situ, without isolation, could further react with a different acid chloride generating product **9n**.

2-Ethylimidazoline **10** was also studied as a substrate to generate nucleophilic *N*,*N*′-diacyl ketene acetals (Table 2). However, the steric hindrance from the methyl group on the β-carbon in ketene acetals **12a–c** blocked the β-carbon's further reaction with benzoyl chlorides. Ketene acetals **12a–c** were not stable to silica-gel column chromatography; in every case, these acetals ring-opened to give products **13a–c**.

Surprisingly, the replacement of the amine hydrogen in **4** with a methyl group dramatically altered the reaction outcome. Thus, 1,2-dimethylimidazoline (**11**) produced the ring-opened vinyl benzoates **14a–k**, where formation of carbon–carbon bonds, carbon–nitrogen bonds, and carbon–oxygen bonds occurred in a one-pot procedure (Table 3). A *Z*-double bond was stereoselectively formed between the methyl carbon at C-2 and benzoyl chloride's

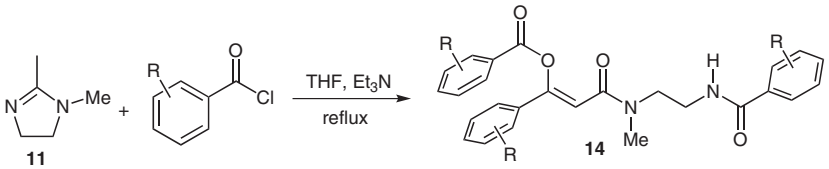
Table 2 Reactions of 2-Ethylimidazoline **10** with Various Benzoyl Chlorides[a]



Entry	Ar	Product	Yield (%)[b]
1	Ph	**13a**	82
2	4-MeC_6H_4	**13b**	87
3	4-ClC_6H_4	**13c**	83

[a] The ratio of **10**/acid chloride/Et_3N = 1:3.5:4.
[b] Isolated yield after column chromatography.

Table 3 Reactions of 1,2-Dimethylimidazoline **11** with Various Benzoyl Chlorides[a]



Entry	R	Time (h)	Product	Yield (%)[b]
1	H	3	**14a**	74
2	*p*-MeO	3	**14b**	63
3	*p*-Me	3	**14c**	65
4	*p*-Cl	3	**14d**	70
5	*p*-F	6	**14e**	56
6	*o*-Me	3	**14f**	60
7	*o*-F	6	**14g**	36
8	*m*-Cl	6	**14h**	52
9	*m*-Me	6	**14i**	60
10	*m*-MeO	6	**14j**	55
11	*m*-F	3	**14k**	43

[a] The ratio of **11**/acid chloride/Et_3N = 1:3.5:4.
[b] Isolated yield after column chromatography.

carbonyl carbon in all examples (**14a–k**); no *E*-isomer was ever observed in the NMR spectra of ring-opened products **14a–k**. The X-ray crystal structure of **14a** was obtained and is shown in Figure 2.[29–31]

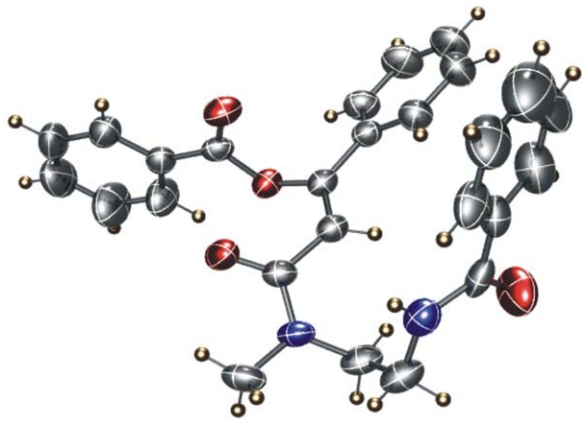
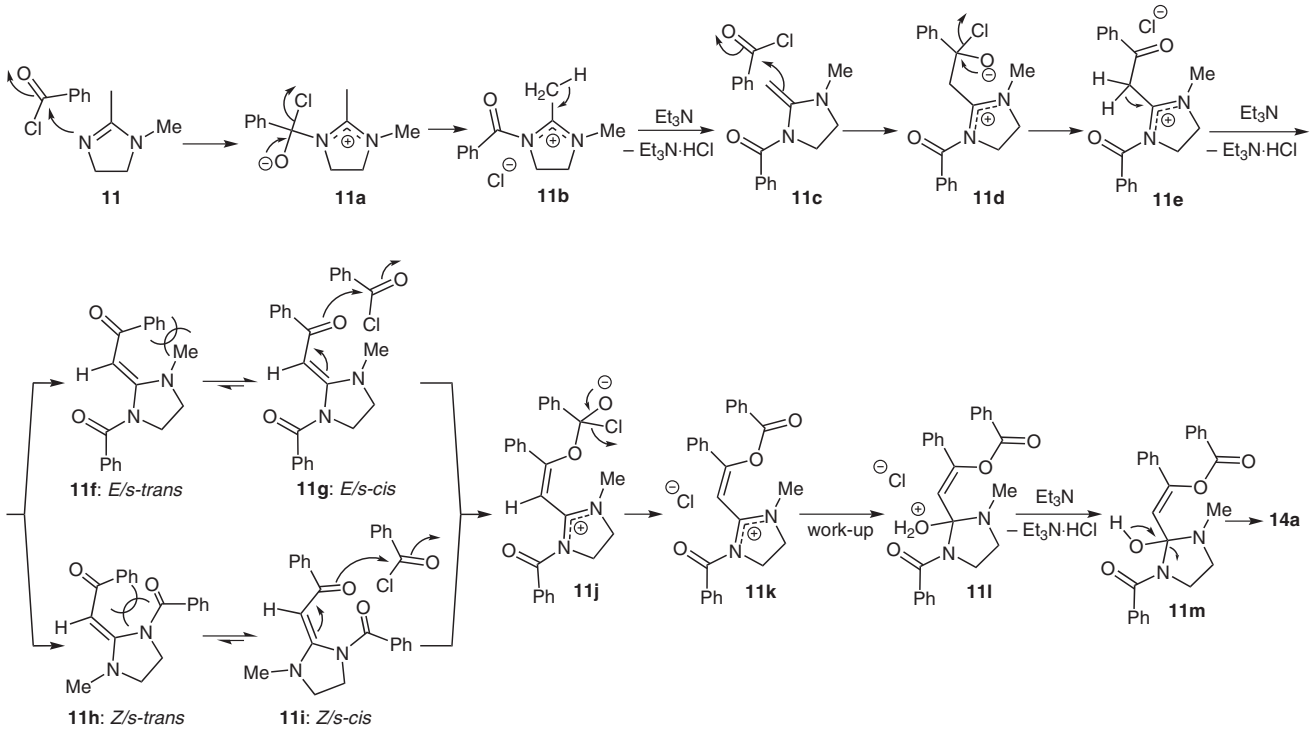


Figure 2 X-ray crystal structure of compound **14a** (gray: C; red: O; blue: N)

The mechanism shown in Scheme 7 accounts for the reaction cascade and the *Z*-stereoselectivity observed during the formation of **14a**. The N-acylation of **11** and deprotonation of **11b** generates *N*-benzoyl-*N*′-methyl ketene-*N*,*N*′-acetal (**11c**). The β-carbon in **11c**, which is activated by two nitrogens, attacks a second benzoyl chloride, giving the zwitterion **11d**. Loss of chloride, followed by deprotonation of **11e**, gives diacylated products **11f–i** with both *E*- and *Z*-geometries about the C=C double bond, and *s-cis*/*s-trans* conformations about the α,β-unsaturated carbonyl group. Steric hindrance between the phenyl group and the N-substituents of the imidazoline ring strongly favors *s-cis* conformers **11g** and **11i** over *s-trans* conformers **11f** and **11h** (by 9.06 and 6.50 kcal/mol, respectively, by Gaussian 03/DFT/B3LYP/6-31g computations). These predominant *s-cis* conformations of **11g** or **11i** determine the formation of the *Z*-double bond geometry in the final product **14a**.

The β-keto oxygen in **11g** and/or **11i** serves as the nucleophile, reacting with a third benzoyl chloride instead of nucleophilic attack by the β-carbon. Steric hindrance exerted by the vicinal substituents and the substantial 1,4-dipolar nature of both **11g/11i**, favor nucleophilic attack by oxygen versus the β-carbon. The *s-cis* conformers **11g** and **11i** must allow substantial conjugation from nitrogen to the carbonyl oxygen although the minimum energy conformations are not completely planar due to steric factors. Chloride loss from the intermediate **11j** gives amidinium salt **11k**. Unlike intermediate **4e** (Scheme 3), which loses a proton to form ring-retained product, amidinium salt **11k** contains no proton that can be removed by triethylamine, so it undergoes ring-opening hydrolysis[32] during work-up, forming benzoate **14a**. The net result of this reaction is the formation of one C=C bond, one C–N bond, one C–O bond, one C=O bond and the cleavage of one C=N bond.



Scheme 7 Proposed mechanism for the formation of **14a**

In conclusion, two tandem reactions of either 2-methylimidazoline or 1,2-dimethylimidazoline with various benzoyl chlorides were demonstrated. These reactions generate highly functionalized compounds and many of these reactions proceed readily under mild conditions, providing moderate to good isolated yields. The reactions of 2-methylimidazolines as multidentate nucleophiles will be further explored.

Melting points were recorded with a Mel-Temp apparatus and are uncorrected. The FT-IR spectra were recorded on a Thermo Nicolet spectrometer as films on KBr plates. The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker model AMX-300 spectrometer operating at 300 MHz for proton and 75 MHz for carbon. Chemical shifts (δ) are reported in ppm units downfield from TMS, which was used as the internal standard for all NMR spectra. Splitting patterns are designed: s, d, t, q and m; these symbols indicate: singlet, doublet, triplet, quartet and multiplet, respectively. All reactions were carried out under nitrogen. Tetrahydrofuran (THF) was distilled from Na metal/benzophenone under nitrogen. MeCN and Et_3N were distilled from CaH_2 under nitrogen. CH_2Cl_2 was pre-dried with $CaCl_2$ and then distilled from CaH_2 under nitrogen. The starting substrates, 2-methylimidazoline (**4**) and 1,2-dimethylimidazoline (**11**), were prepared according to literature procedures.[1,33] All other commercially obtained reagents were used as received. The silica gel used for the column chromatography was purchased from Aldrich (70–230 mesh, 60 Å).

[2-(2-Oxo-2-phenylethylidene)imidazolidine-1,3-diyl]bis(phenylmethanone) (9a)

To a stirred solution of benzoyl chloride (0.492 g, 3.5 mmol) in THF (10 mL), Et_3N (0.405 g, 4 mmol) was added at r.t. under nitrogen. 2-Methylimidazoline (**4**; 0.084 g, 1 mmol) was dissolved in THF (2 mL) and then added dropwise at r.t. into the above solution. The reaction system was then refluxed for 3 h. After cooling to r.t., the solvent was removed by rotary evaporation. CH_2Cl_2 (15 mL) was added to the residue to give a brown solution, which was washed with sat. aq $NaHCO_3$ (3 × 15 mL), dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (silica gel; hexane–EtOAc, 3:1→2:1) to give **9a**.

Yield: 282 mg (71%); yellow solid; mp 188–190 °C; R_f = 0.42 (hexane–EtOAc, 1:1).

IR (KBr): 1705, 1668, 1645, 1577, 1555 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76–7.29 (m, 16 H, ArH and C=CH), 3.92 (m, 4 H, CH_2CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.6 (=CHCOPh), 169.6 (NCOPh), 169.5 (NCOPh), 145.9 (C=CH), 139.3 (ArC), 135.6 (ArC), 134.2 (ArC), 131.9 (ArC), 131.6 (ArC), 131.2 (ArC), 128.8 (ArC), 128.2 (ArC), 127.9 (ArC), 127.0 (ArC), 95.5 (C=CH), 47.6 (NCH_2), 47.2 (NCH_2).

HRMS: *m/z* $[M]^+$ calcd for $C_{25}H_{20}N_2O_3$: 396.1474; found: 396.1462.

{2-[2-(4-Chlorophenyl)-2-oxoethylidene]imidazolidine-1,3-diyl}bis[(4-chlorophenyl)methanone] (9b)

The title compound **9b** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 4-chlorobenzoyl chloride (0.613 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 3:1→2:1).

Yield: 325 mg (65%); yellow solid; mp 195–197 °C; R_f = 0.26 (hexane–EtOAc, 2:1).

IR (KBr): 1695, 1665, 1634, 1588, 1571 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.28 (m, 13 H, ArH and C=CH), 3.90 (m, 4 H, CH_2CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.2 (=CHCOPh), 168.6 (NCOPh), 168.4 (NCOPh), 146.2 (C=CH), 138.4 (ArC), 138.2 (ArC), 137.8 (ArC), 137.4 (ArC), 133.7 (ArC), 132.4 (ArC), 130.2 (ArC), 129.2 (ArC), 129.0 (ArC), 128.6 (ArC), 128.4 (ArC), 95.0 (C=CH), 47.5 (NCH_2), 47.4 (NCH_2).

HRMS: *m/z* $[M]^+$ calcd for $C_{25}H_{17}Cl_3N_2O_3$: 498.0305; found: 498.0318.

[2-(2-Oxo-2-*p*-tolylethylidene)imidazolidine-1,3-diyl]bis(*p*-tolylmethanone) (9c)

The title compound **9c** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 4-methylbenzoyl chloride (0.541 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 3:1→2:1).

Yield: 255 mg (58%); yellow solid; mp 168–170 °C; R_f = 0.50 (hexane–EtOAc, 1:1).

IR (KBr): 1705, 1664, 1606 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 7.9 Hz, 2 H, ArH), 7.56 (d, *J* = 7.9 Hz, 2 H, ArH), 7.48 (d, *J* = 7.9 Hz, 2 H, ArH), 7.25 (d, *J* = 7.9 Hz, 2 H, ArH), 7.19 (s, 1 H, C=C*H*), 7.14 (d, *J* = 7.9 Hz, 2 H, ArH), 7.07 (d, *J* = 7.9 Hz, 2 H, ArH), 3.87 (m, 4 H, CH_2CH_2), 2.39 (s, 3 H, ArCH_3), 2.31 (s, 3 H, ArCH_3), 2.30 (s, 3 H, ArCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.2 (=CH*C*OPh), 169.7 (N*C*OPh), 169.5 (N*C*OPh), 145.9 (*C*=CH), 142.3 (Ar*C*), 141.9 (Ar*C*), 141.6 (Ar*C*), 136.8 (Ar*C*), 132.8 (Ar*C*), 131.4 (Ar*C*), 129.2 (Ar*C*), 128.9 (Ar*C*), 128.7 (Ar*C*), 128.5 (Ar*C*), 127.7 (Ar*C*), 127.1 (Ar*C*), 95.3 (C=*C*H), 47.6 (NCH_2), 47.2 (NCH_2), 21.3 (ArCH_3).

HRMS: *m/z* $[M]^+$ calcd for $C_{28}H_{26}N_2O_3$: 438.1943; found: 438.1930.

{2-[2-(4-Methoxyphenyl)-2-oxoethylidene]imidazolidine-1,3-diyl}bis[(4-methoxyphenyl)methanone] (9d)

The title compound **9d** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 4-methoxylbenzoyl chloride (0.597 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 1:1→1:2).

Yield: 355 mg (73%); yellow solid; mp 93–95 °C; R_f = 0.18 (hexane–EtOAc, 1:1).

IR (KBr): 1693, 1660, 1651, 1598, 1573 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.57 (m, 6 H, ArH), 7.16 (s, 1 H, C=CH), 6.96–6.76 (m, 6 H, ArH), 3.90 (m, 4 H, CH_2CH_2), 3.83 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.3 (=CH*C*OPh), 169.4 (NCOPh), 169.3 (NCOPh), 162.4 (Ar*C*), 162.2 (Ar*C*), 161.9 (Ar*C*), 146.1 (*C*=CH), 132.3 (Ar*C*), 131.0 (Ar*C*), 129.7 (Ar*C*), 129.4 (Ar*C*), 127.5 (Ar*C*), 126.3 (Ar*C*), 113.8 (Ar*C*), 113.4 (Ar*C*), 113.0 (Ar*C*), 94.8 (C=*C*H), 55.3 (OCH_3), 55.24 (OCH_3), 55.16 (OCH_3), 47.96 (NCH_2), 47.58 (NCH_2).

{2-[2-(4-Fluorophenyl)-2-oxoethylidene]imidazolidine-1,3-diyl}bis[(4-fluorophenyl)methanone] (9e)

The title compound **9e** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 4-fluorobenzoyl chloride (0.555 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 2:1).

Yield: 338 mg (75%); yellow solid; mp 143–145 °C; R_f = 0.26 (hexane–EtOAc, 2:1).

IR (KBr): 1690, 1682, 1660, 1640, 1594 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.60 (m, 6 H, ArH), 7.26 (s, 1 H, C=CH), 7.21–6.98 (m, 6 H, ArH), 3.92 (m, 4 H, CH_2CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.39 (=CH*C*OPh), 168.76 (NCOPh), 168.53 (NCOPh), 164.98 (d, $^1J_{CF}$ = 252.8 Hz, Ar*C*), 164.86 (d, $^1J_{CF}$ = 253.7 Hz, Ar*C*), 164.28 (d, $^1J_{CF}$ = 253.4 Hz, Ar*C*), 146.16 (*C*=CH), 135.41 (d, $^4J_{CF}$ = 2.9 Hz, Ar*C*), 131.50 (d, $^4J_{CF}$ = 3.5 Hz, Ar*C*), 131.34 (d, $^3J_{CF}$ = 9.1 Hz, Ar*C*), 129.6 (d, $^3J_{CF}$ = 8.8 Hz, Ar*C*), 130.09 (d, $^3J_{CF}$ = 9.0 Hz, Ar*C*), 130.13 (d, $^4J_{CF}$ = 3.3 Hz, Ar*C*), 116.06 (d, $^2J_{CF}$ = 22.1 Hz, Ar*C*), 115.49 (d, $^2J_{CF}$ = 22.1 Hz, Ar*C*), 115.12 (d, $^2J_{CF}$ = 21.8 Hz, Ar*C*), 95.11 (C=*C*H), 47.7 (NCH_2), 47.6 (NCH_2).

{2-[2-(3-Chlorophenyl)-2-oxoethylidene]imidazolidine-1,3-diyl}bis[(3-chlorophenyl)methanone] (9f)

The title compound **9f** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 3-chlorobenzoyl chloride (0.613 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 2:1).

Yield: 380 mg (76%); yellow solid; mp 83–85 °C; R_f = 0.29 (hexane–EtOAc, 2:1).

IR (KBr): 1703, 1673, 1651, 1567, 1557 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.22 (m, 13 H, Ar*H* and C=CH), 3.89 (m, 4 H, CH_2CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.22 (=CH*C*OPh), 167.98 (NCOPh), 167.79 (NCOPh), 145.98 (*C*=CH), 140.46 (Ar*C*), 136.80 (Ar*C*), 135.44 (Ar*C*), 134.81 (Ar*C*), 134.16 (Ar*C*), 134.12 (Ar*C*), 131.92 (Ar*C*), 131.67 (Ar*C*), 131.37 (Ar*C*), 130.18 (Ar*C*), 129.54 (Ar*C*), 129.36 (Ar*C*) 128.60 (Ar*C*), 127.52 (Ar*C*), 126.94 (Ar*C*), 126.69 (Ar*C*), 125.57 (Ar*C*), 124.82 (Ar*C*), 94.97 (C=*C*H), 47.40 (NCH_2), 47.22 (NCH_2).

HRMS: *m/z* $[M]^+$ calcd for $C_{25}H_{17}Cl_3N_2O_3$: 498.0305; found: 498.0301.

[2-(2-Oxo-2-*m*-tolylethylidene)imidazolidine-1,3-diyl]bis(*m*-tolylmethanone) (9g)

The title compound **9g** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 3-methylbenzoyl chloride (0.541 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 2:1).

Yield: 316 mg (72%); yellow solid; mp 81–83 °C; R_f = 0.27 (hexane–EtOAc, 2:1).

IR (KBr): 1699, 1669, 1603, 1584, 1558 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.11 (m, 13 H, ArH and C=CH), 3.86 (m, 4 H, CH_2CH_2), 2.34 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.47 (=CH*C*OPh), 169.45 (NCOPh), 169.21 (NCOPh), 145.53 (*C*=CH), 138.96 (Ar*C*), 138.26 (Ar*C*), 137.54 (Ar*C*), 137.11 (Ar*C*), 135.28 (Ar*C*), 133.78 (Ar*C*), 132.22 (Ar*C*), 131.94 (Ar*C*), 131.45 (Ar*C*), 128.95 (Ar*C*), 128.21 (Ar*C*), 127.77 (Ar*C*), 127.62 (Ar*C*), 127.42 (Ar*C*), 127.07 (Ar*C*), 125.49 (Ar*C*), 124.39 (Ar*C*), 123.53 (Ar*C*), 94.99 (C=*C*H), 47.31 (NCH_2), 46.89 (NCH_2), 20.85 (CH_3), 20.78 (CH_3), 20.75 (CH_3).

{2-[2-(3-Methoxyphenyl)-2-oxoethylidene]imidazolidine-1,3-diyl}bis[(3-methoxyphenyl)methanone] (9h)

The title compound **9h** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 3-methoxylbenzoyl chloride (0.597 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 2:1→1:1).

Yield: 365 mg (75%); yellow solid; mp 140–142 °C; R_f = 0.43 (hexane–EtOAc, 1:1).

IR (KBr): 1707, 1670, 1653, 1560 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–6.93 (m, 13 H, ArH and C=CH), 3.84 (m, 4 H, CH_2CH_2), 3.77 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.14 (=CH*C*OPh), 169.16 (NCOPh), 168.92 (NCOPh), 159.39 (Ar*C*), 159.10 (Ar*C*), 159.05 (Ar*C*), 145.42 (*C*=CH), 140.51 (Ar*C*), 136.57 (Ar*C*), 135.15 (Ar*C*), 129.68 (Ar*C*), 129.02 (Ar*C*), 128.69 (Ar*C*), 120.68 (Ar*C*), 119.93 (Ar*C*), 118.53 (Ar*C*), 118.12 (Ar*C*), 117.74 (Ar*C*), 116.68 (Ar*C*), 113.62 (Ar*C*), 111.91 (Ar*C*), 111.52 (Ar*C*), 95.30 (C=*C*H), 55.07

(O*C*H$_3$), 55.01 (O*C*H$_3$), 54.90 (O*C*H$_3$), 47.59 (N*C*H$_2$), 47.20 (N*C*H$_2$).

{2-[2-(3-Fluorophenyl)-2-oxoethylidene]imidazolidine-1,3-diyl}bis[(3-fluorophenyl)methanone] (9i)

The title compound **9i** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 3-fluorobenzoyl chloride (0.555 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 2:1).

Yield: 342 mg (76%); yellow solid; mp 88–90 °C; R_f = 0.29 (hexane–EtOAc, 2:1).

IR (KBr): 1703, 1672, 1611, 1586, 1556 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.52–7.08 (m, 13 H, ArH and C=CH), 3.89 (m, 4 H, CH_2CH_2).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 186.3 (=CH*C*OPh), 168.17 (d, $^4J_{CF}$ = 2.5 Hz, NCOPh), 167.98 (d, $^4J_{CF}$ = 2.6 Hz, NCOPh), 162.45 (d, $^1J_{CF}$ = 246.9 Hz, Ar*C*), 162.36 (d, $^1J_{CF}$ = 249.5 Hz, Ar*C*), 162.08 (d, $^1J_{CF}$ = 247.9 Hz, Ar*C*), 145.96 (*C*=CH), 141.22 (d, $^3J_{CF}$ = 6.2 Hz, Ar*C*), 137.21 (d, $^3J_{CF}$ = 6.9 Hz, Ar*C*), 135.91 (d, $^3J_{CF}$ = 7.0 Hz, Ar*C*), 130.73 (d, $^3J_{CF}$ = 8.0 Hz, Ar*C*), 129.98 (d, $^3J_{CF}$ = 7.8 Hz, Ar*C*), 129.67 (d, $^3J_{CF}$ = 7.6 Hz, Ar*C*), 124.31 (d, $^4J_{CF}$ = 3.0 Hz, Ar*C*), 123.21 (d, $^4J_{CF}$ = 2.8 Hz, Ar*C*), 122.45 (d, $^4J_{CF}$ = 3.2 Hz, Ar*C*), 119.05 (d, $^2J_{CF}$ = 21.2 Hz, Ar*C*), 118.71 (d, $^2J_{CF}$ = 21.5 Hz, Ar*C*), 118.37 (d, $^2J_{CF}$ = 21.1 Hz, Ar*C*), 115.72 (d, $^2J_{CF}$ = 23.0 Hz, Ar*C*), 114.28 (d, $^2J_{CF}$ = 22.3 Hz, Ar*C*), 114.15 (d, $^2J_{CF}$ = 23.3 Hz, Ar*C*), 95.16 (C=*C*H), 47.60 (NCH$_2$), 47.42 (NCH$_2$).

{2-[2-(3-Bromophenyl)-2-oxoethylidene]imidazolidine-1,3-diyl}bis[(3-bromophenyl)methanone] (9j)

The title compound **9j** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 3-bromobenzoyl chloride (0.768 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 2:1).

Yield: 494 mg (78%); yellow solid; mp 152–154 °C; R_f = 0.30 (hexane–EtOAc, 2:1).

IR (KBr): 1690, 1646, 1587, 1551 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.83–7.17 (m, 13 H, ArH and C=CH), 3.90 (m, 4 H, CH_2CH_2).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 186.12 (=CH*C*OPh), 167.82 (NCOPh), 167.65 (NCOPh), 145.97 (*C*=CH), 140.64 (Ar*C*), 136.98 (Ar*C*), 135.63 (Ar*C*), 134.86 (Ar*C*), 134.62 (Ar*C*), 134.35 (Ar*C*), 131.49 (Ar*C*), 130.47 (Ar*C*), 130.42 (Ar*C*), 129.83 (Ar*C*), 129.81 (Ar*C*), 129.66 (Ar*C*), 127.17 (Ar*C*), 126.06 (Ar*C*), 125.30 (Ar*C*), 122.82 (Ar*C*), 122.33 (Ar*C*), 122.14 (Ar*C*), 94.96 (C=*C*H), 47.39 (NCH$_2$), 47.19 (NCH$_2$).

HRMS: *m*/*z* [M]$^+$ calcd for $C_{25}H_{17}Br_3N_2O_3$: 629.8789; found: 629.8774.

{2-[2-(2-Chlorophenyl)-2-oxoethylidene]imidazolidine-1,3-diyl}bis[(2-chlorophenyl)methanone] (9k)

The title compound **9k** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 2-chlorobenzoyl chloride (0.613 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; toluene–EtOAc, 10:1→6:1).

Yield: 345 mg (69%); yellow solid; mp 77–79 °C; R_f = 0.36 (toluene–EtOAc, 6:1).

IR (KBr): 1667, 1651, 1589, 1567 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.69–7.02 (m, 13 H, ArH and C=CH), 4.10 (br, 2 H, CH$_2$), 3.73 (br, 2 H, CH$_2$).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 189.31 (=CH*C*OPh), 167.39 (NCOPh), 166.45 (NCOPh), 145.71 (*C*=CH), 140.31 (Ar*C*), 135.54 (Ar*C*), 134.09 (Ar*C*), 132.18 (Ar*C*), 131.48 (Ar*C*), 131.35 (Ar*C*), 130.89 (Ar*C*), 130.74 (Ar*C*), 130.26 (Ar*C*), 130.05 (Ar*C*), 129.57 (Ar*C*), 129.03 (Ar*C*), 127.67 (Ar*C*), 127.20 (Ar*C*), 126.88 (Ar*C*), 126.35 (Ar*C*), 99.01 (C=*C*H), 45.77 (NCH$_2$), 45.25 (NCH$_2$).

{2-[2-(2-Fluorophenyl)-2-oxoethylidene]imidazolidine-1,3-diyl}bis[(2-fluorophenyl)methanone] (9l)

The title compound **9l** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 2-fluorobenzoyl chloride (0.613 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 3:1→5:3).

Yield: 306 mg (68%); yellow liquid; R_f = 0.40 (hexane–EtOAc, 1:1).

IR (KBr): 1672, 1611, 1581, 1556 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.69–7.00 (m, 13 H, ArH and C=CH), 4.08 (t, *J* = 7.0 Hz, 4 H, CH$_2$), 3.83 (t, *J* = 7.0 Hz, 4 H, CH$_2$).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 185.72 (d, $^3J_{CF}$ = 2.2 Hz, =CH*C*OPh), 165.67 (NCOPh), 165.12 (NCOPh), 160.25 (d, $^1J_{CF}$ = 253.8 Hz, Ar*C*), 158.63 (d, $^1J_{CF}$ = 250.7 Hz, Ar*C*), 157.71 (d, $^1J_{CF}$ = 249.3 Hz, Ar*C*), 146.00 (*C*=CH), 132.77 (d, $^3J_{CF}$ = 8.8 Hz, Ar*C*), 132.73 (d, $^3J_{CF}$ = 8.5 Hz, Ar*C*), 132.62 (d, $^3J_{CF}$ = 7.9 Hz, Ar*C*), 131.77 (d, $^4J_{CF}$ = 1.8 Hz, Ar*C*), 130.02 (d, $^4J_{CF}$ = 2.4 Hz, Ar*C*), 128.53 (d, $^4J_{CF}$ = 2.9 Hz, Ar*C*), 128.17 (d, $^2J_{CF}$ = 12.3 Hz, Ar*C*), 124.91 (d, $^3J_{CF}$ = 3.4 Hz, Ar*C*), 124.08 (d, $^3J_{CF}$ = 3.7 Hz, Ar*C*), 124.00 (d, $^2J_{CF}$ = 16.5 Hz, Ar*C*), 123.68 (d, $^3J_{CF}$ = 3.5 Hz, Ar*C*), 122.50 (d, $^2J_{CF}$ = 12.6 Hz, Ar*C*), 116.119 (d, $^2J_{CF}$ = 20.9 Hz, Ar*C*), 115.98 (d, $^2J_{CF}$ = 23.2 Hz, Ar*C*), 115.28 (d, $^2J_{CF}$ = 22.2 Hz, Ar*C*), 98.29 (C=*C*H), 46.06 (NCH$_2$), 45.67 (NCH$_2$).

{2-[2-(2-Bromophenyl)-2-oxoethylidene]imidazolidine-1,3-diyl}bis[(2-bromophenyl)methanone] (9m)

The title compound **9m** was prepared using 2-methylimidazoline (**4**; 0.084 g, 1 mmol) and 2-bromobenzoyl chloride (0.768 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; toluene–EtOAc, 6:1).

Yield: 443 mg (70%); yellow solid; mp 86–87 °C; R_f = 0.56 (toluene–EtOAc, 3:1).

IR (KBr): 1682, 1651, 1588, 1567 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.64–7.02 (m, 13 H, ArH and C=CH), 4.01 (br, 2 H, CH$_2$), 3.69 (br, 2 H, CH$_2$).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 189.93 (=CH*C*OPh), 167.43 (NCOPh), 166.85 (NCOPh), 145.07 (*C*=CH), 141.97 (Ar*C*), 137.41 (Ar*C*), 136.13 (Ar*C*), 133.11 (Ar*C*), 132.96 (Ar*C*), 132.14 (Ar*C*), 131.43 (Ar*C*), 131.30 (Ar*C*), 130.87 (Ar*C*), 129.01 (Ar*C*), 128.81 (Ar*C*), 128.08 (Ar*C*), 127.30 (Ar*C*), 127.08 (Ar*C*), 126.80 (Ar*C*), 118.86 (Ar*C*), 118.79 (Ar*C*), 117.90 (Ar*C*), 98.82 (C=*C*H), 45.81 (NCH$_2$), 45.37 (NCH$_2$).

[2-(2-Oxo-2-*p*-tolylethylidene)imidazolidine-1,3-diyl]bis(phenylmethanone) (9n)

Yellow solid; mp 195–196 °C.

IR (KBr): 1677, 1657, 1638, 1604, 1537 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.77–7.09 (m, 15 H, ArH and C=CH), 3.99–3.55 (m, 4 H, CH_2CH_2), 2.33 (s, 3 H, PhCH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 187.2 (=CH*C*OAr), 169.6 (NCOPh), 169.5 (NCOPh), 145.5 (*C*=CH), 142.2 (Ar*C*), 136.3 (Ar*C*), 135.6 (Ar*C*), 134.1 (Ar*C*), 131.9 (Ar*C*), 131.2 (Ar*C*), 128.8 (Ar*C*), 128.7 (Ar*C*), 128.2 (Ar*C*), 127.8 (Ar*C*), 127.0 (Ar*C*), 95.8 (C=*C*H), 47.6 (NCH$_2$), 47.2 (NCH$_2$), 21.4 (ArCH$_3$).

(2-Methyl-4,5-dihydro-1*H*-imidazol-1-yl)(phenyl)methanone (4c)

White solid; mp 155–157 °C.

IR (KBr): 1665, 1632, 1557 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.38 (m, 5 H, ArH), 3.87–3.72 (m, 4 H, CH_2CH_2), 2.18 (s, 3 H, CCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.8 (NCOPh), 157.8 (NCN), 135.5 (Ar*C*), 130.2 (Ar*C*), 127.7 (Ar*C*), 126.4 (Ar*C*), 52.0 (NCH_2), 48.2 (NCH_2), 17.9 (CCH_3).

_N_-Acetyl-_N_-(2-benzamidoethyl)benzamide (5)
White solid; mp 115–116 °C (Lit.[23a] 115 °C).

IR (KBr): 3316, 1694, 1686, 1636, 1527 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.42 (m, 10 H, ArH), 7.11 (br, 1 H, NH), 4.12 (t, *J* = 5.2 Hz, 2 H, CH_2CH_2), 3.66 (q, *J* = 5.2 Hz, 2 H, CH_2CH_2), 2.10 (s, 3 H, CCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7 (CH_3CO), 174.1 (PhCON), 167.4 (PhCONH), 134.9 (Ar*C*), 133.8 (Ar*C*), 132.8 (Ar*C*), 131.3 (Ar*C*), 128.8 (Ar*C*), 128.5 (Ar*C*), 128.4 (Ar*C*), 126.8 (Ar*C*), 45.3 (NCH_2), 39.9 ($NHCH_2$), 26.2 (CH_3CO).

_N_-(2-Benzamidoethyl)-_N_-propionylbenzamide (13a)
Colorless liquid.

IR (KBr): 3345, 1683, 1660, 1601, 1537 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.64 (m, 11 H, ArH and NH), 4.08 (t, *J* = 5.5 Hz, 2 H, CH_2CH_2), 3.63 (q, *J* = 5.5 Hz, 2 H, CH_2CH_2), 2.36 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 1.02 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.0 (CH_2CO), 174.4 (PhCON), 167.3 (PhCONH), 135.0 (Ar*C*), 133.7 (Ar*C*), 132.4 (Ar*C*), 131.1 (Ar*C*), 128.6 (Ar*C*), 128.2 (Ar*C*), 128.1 (Ar*C*), 126.7 (Ar*C*), 45.2 (NCH_2), 39.7 ($NHCH_2$), 31.4 (CH_2CO), 9.4 (CH_3CH_2).

4-Methyl-_N_-[2-(4-methylbenzamido)ethyl]-_N_-propionylbenzamide (13b)
White solid; mp 70–72 °C.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.20 (m, 9 H, ArH and NH), 4.09 (t, *J* = 5.3 Hz, 2 H, CH_2CH_2), 3.63 (q, *J* = 5.3 Hz, 2 H, CH_2CH_2), 2.39 (s, 6 H, $ArCH_3$), 2.33 (q, *J* = 7.3 Hz, CH_2CH_3, 2 H), 1.04 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.2 (CH_2CO), 174.7 (PhCON), 167.3 (PhCONH), 143.7 (Ar*C*), 141.6 (Ar*C*), 132.2 (Ar*C*), 131.0 (Ar*C*), 129.5 (Ar*C*), 129.0 (Ar*C*), 128.7 (Ar*C*), 126.8 (Ar*C*), 45.4 (NCH_2), 39.9 ($NHCH_2$), 31.6 (CH_2CO), 21.5 ($ArCH_3$), 21.3 ($ArCH_3$), 9.6 (CH_3CH_2).

IR (KBr): 3301, 1688, 1636, 1609, 1537 cm^{-1}.

4-Chloro-_N_-[2-(4-chlorobenzamido)ethyl]-_N_-propionylbenzamide (13c)
White solid; mp 97–99 °C.

IR (KBr): 3346, 1660, 1595, 1537 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.34 (m, 9 H, ArH and NH), 4.08 (t, *J* = 5.5 Hz, 2 H, CH_2CH_2), 3.62 (q, *J* = 5.5 Hz, 2 H, CH_2CH_2), 2.39 (q, *J* = 7.3 Hz, 2 H, CH_2CH_3), 1.05 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.8 (CH_2CO), 173.5 (PhCON), 166.4 (PhCONH), 138.9 (Ar*C*), 137.5 (Ar*C*), 133.3 (Ar*C*), 132.0 (Ar*C*), 129.6 (Ar*C*), 129.0 (Ar*C*), 128.5 (Ar*C*), 128.2 (Ar*C*), 45.2 (NCH_2), 39.7 ($NHCH_2$), 31.3 (CH_2CO), 9.4 (CH_3CH_2).

(_Z_)-3-[(2-Benzamidoethyl)(methyl)amino]-3-oxo-1-phenylprop-1-enyl Benzoate (14a)
The title compound **14a** was prepared using 1,2-dimethylimidazoline (**11**; 0.098 g, 1 mmol) and benzoyl chloride (0.492 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–acetone, 3:1→2:1). Both the ^1H and ^{13}C NMR spectra of **14a** confirmed the presence of two rotational conformations, which interconvert slowly on the NMR time scale, due to restricted rotation about an amide carbonyl carbon to nitrogen bond. These conformations were present in a 2.87:1 ratio based on the relative integral areas of the 3.21 and 2.87 ppm resonances of the N-CH_3 group in the ^1H NMR spectrum.

Yield: 318 mg (74%); white solid; mp 157–159 °C; R_f = 0.39 (hexane–acetone, 1:1).

IR (KBr): 3329, 1728, 1650, 1613 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.14 and 8.09 (2 × d, *J* = 7.7 Hz and *J* = 7.6 Hz, 2 H, NH and ArH), 7.75–7.24 (m, 14 H, ArH), 6.63 and 6.55 (s, 1 H, COCH=C), 3.70 and 3.61 (m, 4 H, CH_2CH_2), 3.21 and 2.87 (2 × s, 3 H, NCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.10 (HN*C*OPh), 167.24 (HN*C*OPh), 166.77 (*C*OCH=C), 164.90 (*C*OCH=C), 164.24 [CH=*C*(Ph)O], 163.95 [CH=*C*(Ph)O], 153.54 (Ph*C*OO), 152.98 (Ph*C*OO), 133.80 (Ar*C*), 133.74 (Ar*C*), 133.67 (Ar*C*), 133.65 (Ar*C*), 133.57 (Ar*C*), 131.35 (Ar*C*), 131.10 (Ar*C*), 130.30 (Ar*C*), 130.25 (Ar*C*), 130.10 (Ar*C*), 130.06 (Ar*C*), 129.07 (Ar*C*), 128.76 (Ar*C*), 128.69 (Ar*C*), 128.64 (Ar*C*), 128.58 (Ar*C*), 128.29 (Ar*C*), 128.21 (Ar*C*), 127.18 (Ar*C*), 126.88 (Ar*C*), 125.53 (Ar*C*), 125.45 (Ar*C*), 108.33 (CO*C*H=C), 107.07 (CO*C*H=C), 49.52 [CON(CH_3)CH_2], 47.26 [CON(CH_3)CH_2], 39.25 (CH_2NHCOPh), 38.46 (CH_2NHCOPh), 37.09 [CON(CH_3)CH_2], 33.77 [CON(CH_3)CH_2].

HRMS: *m*/*z* $[M]^+$ calcd for $C_{26}H_{24}N_2O_4$: 428.1736; found: 428.1743.

(_Z_)-3-{[2-(4-Methoxybenzamido)ethyl](methyl)amino}-1-(4-methoxyphenyl)-1-(4-methoxyphenylcarbonyloxy)-3-oxoprop-1-ene (14b)
The title compound **14b** was prepared using 1,2-dimethylimidazoline (**11**; 0.098 g, 1 mmol) and 4-methoxybenzoyl chloride (0.597 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 3:1→1:1). The ratio of the two rotational conformations was 2.84:1 based on the relative integrals of the 3.19 and 2.87 ppm resonances of the ^1H NMR spectrum.

Yield: 326 mg (63%); white solid; mp 151–153 °C; R_f = 0.21 (hexane–actone, 1:1).

IR (KBr): 3275, 1721, 1650, 1602 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.10 and 8.01 (2 × d, *J* = 8.5 Hz and *J* = 8.5 Hz, 2 H, NH and ArH), 7.70 (m, 3 H, ArH), 7.53 and 7.41 (2 × d, *J* = 8.6 Hz and *J* = 8.5 Hz, 2 H, ArH), 6.94–6.70 (m, 6 H, ArH), 6.52 and 6.42 (s, 1 H, COCH=C), 3.84, 3.82, 3.81, 3.78 and 3.76 (5 × s, 9 H, CH_3OC), 3.59 (m, 4 H, CH_2CH_2), 3.19 and 2.87 (2 × s, 3 H, NCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.51 (HNCOAr), 167.25 (HNCOAr), 166.69 (*C*OCH=C), 165.14 (*C*OCH=C), 163.95 (CH_3O*C*), 163.89 [CH=*C*(Ar)O], 163.86 [CH=*C*(Ar)O], 163.54 (CH_3O*C*), 161.86 (CH_3O*C*), 161.64 (CH_3O*C*), 161.10 (CH_3O*C*), 160.90 (CH_3O*C*), 153.49 (Ar*C*OO), 152.90 (Ar*C*OO), 132.41 (Ar*C*), 132.20 (Ar*C*), 129.02 (Ar*C*), 128.63 (Ar*C*), 127.06 (Ar*C*), 126.95 (Ar*C*), 126.23 (Ar*C*), 126.20 (Ar*C*), 126.13 (Ar*C*), 126.06 (Ar*C*), 121.49 (Ar*C*), 120.97 (Ar*C*), 114.05 (Ar*C*), 113.86 (Ar*C*), 113.79 (Ar*C*), 113.30 (Ar*C*), 113.23 (Ar*C*), 106.37 (CO*C*H=C), 104.91 (CO*C*H=C), 55.44 (CH_3OC), 55.31 (CH_3OC), 55.23 (CH_3OC), 55.16 (CH_3OC), 55.11 (CH_3OC), 49.70 [CON(CH_3)CH_2], 47.32 [CON(CH_3)CH_2], 39.39 (CH_2NHCOAr), 38.51 (CH_2NHCOAr), 37.03 [CON(CH_3)CH_2], 33.83 [CON(CH_3)CH_2].

(*Z*)-3-{[2-(4-Methylbenzamido)ethyl](methyl)amino}-1-(4-methylphenyl)-1-(4-methylphenylcarbonyloxy)-3-oxoprop-1-ene (14c)

The title compound **14c** was prepared using 1,2-dimethylimidazoline (**11**; 0.098 g, 1 mmol) and 4-methylbenzoyl chloride (0.541 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–acetone, 4:1→3:1). The ratio of the two rotational conformations was 2.92:1 based on the relative integrals of the 3.19 and 2.87 ppm resonances of the ^{1}H NMR spectrum.

Yield: 306 mg (65%); white solid; mp 158–160 °C; R_f = 0.46 (hexane–acetone, 1:1).

IR (KBr): 3360, 1735, 1640, 1607 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 and 7.97 (2 × d, *J* = 7.8 Hz and *J* = 8.0 Hz, 2 H, NH and ArH), 7.63–7.02 (m, 11 H , ArH), 6.57 and 6.48 (2 × s, 1 H, COC*H*=C), 3.69–3.56 (m, 4 H, CH_2CH_2), 3.19 and 2.87 (2 × s, 3 H, NCH_3), 2.41, 2.40, 2.38, 2.36 and 2.33 (5 × s, 9 H, CH_3Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.94 (HNCOPh), 167.16 (HNCOPh), 166.91 (*C*OCH=C), 165.07 (*C*OCH=C), 164.27 [CH=*C*(Ar)O], 163.96 [CH=*C*(Ar)O], 153.58 (Ar*C*OO), 153.10 (Ar*C*OO), 144.49 (Ar*C*), 141.53 (Ar*C*), 141.16 (Ar*C*), 140.44 (Ar*C*), 140.16 (Ar*C*), 130.98 (Ar*C*), 130.95 (Ar*C*), 130.33 (Ar*C*), 130.16 (Ar*C*), 129.39 (Ar*C*), 129.28 (Ar*C*), 129.21 (Ar*C*), 128.87 (Ar*C*), 128.79 (Ar*C*), 127.18 (Ar*C*), 126.88 (Ar*C*), 126.46 (Ar*C*), 126.09 (Ar*C*), 125.44 (Ar*C*), 125.37 (Ar*C*), 107.48 (CO*C*H=C), 106.25 (CO*C*H=C), 49.55 [CON(CH_3)*C*H_2], 47.27 [CON(CH_3)*C*H_2], 39.18 (*C*H_2NHCOPh), 38.46 (*C*H_2NHCOPh), 37.02 [CON(*C*H_3)CH_2], 33.80 [CON(*C*H_3)CH_2], 21.65 (CH_3Ar), 21.31 (CH_3Ar), 21.26 (CH_3Ar).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{29}H_{30}N_2NaO_4$: 493.2103; found: 493.2067.

(*Z*)-3-{[2-(4-Chlorobenzamido)ethyl](methyl)amino}-1-(4-chlorophenyl)-1-(4-chlorophenylcarbonyloxy)-3-oxoprop-1-ene (14d)

The title compound **14d** was prepared using 1,2-dimethylimidazoline (**11**; 0.098 g, 1 mmol) and 4-chlorobenzoyl chloride (0.613 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–acetone, 4:1→3:1). The ratio of the two rotational conformations was 3.35:1 based on the relative integrals of the 3.22 and 2.92 ppm resonances of the ^{1}H NMR spectrum.

Yield: 373 mg (70%); white solid; mp 184–185 °C; R_f = 0.65 (hexane–acetone, 1:1).

IR (KBr): 3297, 1750, 1661, 1608 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07–7.17 (m, 13 H, NH and ArH), 6.60 and 6.53 (2 × s, 1 H, COCH=C), 3.70–3.60 (m, 4 H, CH_2CH_2), 3.22 and 2.92 (2 × s, 3 H, NCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.01 (HNCOPh), 166.78 (HNCOPh), 165.96 (*C*OCH=C), 164.46 (*C*OCH=C), 163.46 [CH=*C*(Ar)O], 162.85 [CH=*C*(Ar)O], 152.62 (Ar*C*OO), 152.21 (Ar*C*OO), 140.64 (Ar*C*), 140.50 (Ar*C*), 137.67 (Ar*C*), 137.35 (Ar*C*), 136.49 (Ar*C*), 136.28 (Ar*C*), 131.93 (Ar*C*), 131.85 (Ar*C*), 131.71 (Ar*C*), 131.61 (Ar*C*), 131.35 (Ar*C*), 129.09 (Ar*C*), 129.01 (Ar*C*), 128.84 (Ar*C*), 128.59 (Ar*C*), 128.42 (Ar*C*), 128.29 (Ar*C*), 128.23 (Ar*C*), 127.29 (Ar*C*), 126.81 (Ar*C*), 126.72 (Ar*C*), 126.49 (Ar*C*), 108.60 (CO*C*H=C), 106.64 (CO*C*H=C), 49.60 [CON(CH_3)*C*H_2], 47.25 [CON(CH_3)*C*H_2], 39.70 (*C*H_2NHCOPh), 38.61 (*C*H_2NHCOPh), 36.88 [CON(*C*H_3)CH_2], 33.75 [CON(*C*H_3)CH_2].

(*Z*)-3-{[2-(4-Fluorobenzamido)ethyl](methyl)amino}-1-(4-fluorophenyl)-1-(4-fluorophenylcarbonyloxy)-3-oxoprop-1-ene (14e)

The title compound **14e** was prepared using 1,2-dimethylimidazoline (**11**; 0.098 g, 1 mmol) and 4-fluorobenzoyl chloride (0.555 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–acetone, 4:1→2:1). The ratio of the two rotational conformations was 2.06:1 based on the relative integrals of the 3.16 and 2.78 ppm resonances of the ^{1}H NMR spectrum.

Yield: 269 mg (56%); white solid; mp 143–144 °C; R_f = 0.45 (hexane–acetone, 1:1).

IR (KBr): 3327, 1749, 1645, 1602 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10–8.62 (m, 13 H, NH and ArH), 6.57 and 6.47 (2 × s, 1 H, COCH=C), 3.65–3.51 (m, 4 H, CH_2CH_2), 3.16 and 2.78 (2 × s, 3 H, NCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.85 (HNCOPh), 166.45 (HNCOPh), 165.98 (d, $^1J_{CF}$ = 253.8 Hz, Ar*C*), 165.97 (*C*OCH=C), 164.73 (d, $^1J_{CF}$ = 252.3 Hz, Ar*C*), 164.45 (*C*OCH=C), 164.40 (d, $^1J_{CF}$ = 251.8 Hz, Ar*C*), 164.25 (d, $^1J_{CF}$ = 253.1 Hz, Ar*C*), 163.67 (d, $^1J_{CF}$ = 251.3 Hz, Ar*C*), 163.58 (d, $^1J_{CF}$ = 252.1 Hz, Ar*C*), 163.06 [CH=*C*(Ar)O], 162.58 [CH=*C*(Ar)O], 152.97 (Ar*C*OO), 152.16 (Ar*C*OO), 132.67 (d, $^3J_{CF}$ = 10.6 Hz, Ar*C*), 132.53 (d, $^3J_{CF}$ = 9.8 Hz, Ar*C*), 129.67 (d, $^4J_{CF}$ = 3.0 Hz, Ar*C*), 129.57 (d, $^4J_{CF}$ = 3.2 Hz, Ar*C*), 129.47 (d, $^4J_{CF}$ = 3.0 Hz, Ar*C*), 129.33 (d, $^4J_{CF}$ = 2.7 Hz, Ar*C*), 129.07 (d, $^3J_{CF}$ = 8.9 Hz, Ar*C*), 129.07 (d, $^3J_{CF}$ = 8.9 Hz, Ar*C*), 127.44 (d, $^3J_{CF}$ = 8.6 Hz, Ar*C*), 127.30 (d, $^3J_{CF}$ = 8.9 Hz, Ar*C*), 125.03 (d, $^4J_{CF}$ = 3.0 Hz, Ar*C*), 124.57 (d, $^4J_{CF}$ = 2.9 Hz, Ar*C*), 115.78 (d, $^2J_{CF}$ = 22.1 Hz, Ar*C*), 115.70 (d, $^2J_{CF}$ = 22.2 Hz, Ar*C*), 115.63 (d, $^2J_{CF}$ = 22.3 Hz, Ar*C*), 115.56 (d, $^2J_{CF}$ = 21.5 Hz, Ar*C*), 114.98 (d, $^2J_{CF}$ = 22.8 Hz, Ar*C*), 114.91 (d, $^2J_{CF}$ = 21.6 Hz, Ar*C*), 107.88 (CO*C*H=C), 106.20 (CO*C*H=C), 49.17 [CON(CH_3)*C*H_2], 47.01 [CON(CH_3)*C*H_2], 39.14 (*C*H_2NHCOPh), 38.17 (*C*H_2NHCOPh), 36.67 [CON(*C*H_3)CH_2], 33.27 [CON(*C*H_3)CH_2].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{26}H_{21}F_3N_2O_4$: 482.1453; found: 482.1445.

(*Z*)-3-{[2-(2-Methylbenzamido)ethyl](methyl)amino}-1-(2-methylphenyl)-1-(2-methylphenylcarbonyloxy)-3-oxoprop-1-ene (14f)

The title compound **14f** was prepared using 1,2-dimethylimidazoline (**11**; 0.098 g, 1 mmol) and 2-methylbenzoyl chloride (0.541 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–acetone, 4:1→3:1). The ratio of the two rotational conformations was 2.37:1 based on the relative integrals of the 3.21 and 2.97 ppm resonances of the ^{1}H NMR spectrum.

Yield: 283 mg (60%); white solid; mp 117–119 °C; R_f = 0.53 (hexane–acetone, 1:1).

IR (KBr): 3300, 1739, 1650, 1611 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 and 7.98 (2 × d, *J* = 8.2 Hz and *J* = 8.2 Hz, 1 H, ArH), 7.46–7.04 (m, 11 H, ArH), 6.94 and 6.72 (2 × s, 1 H, NH), 6.18 and 6.09 (2 × s, 1 H, COCH=C), 3.71–3.58 (m, 4 H, CH_2CH_2), 3.21 and 2.97 (2 × s, 3 H, NCH_3), 2.48, 2.46, 2.45, 2.41 and 2.33 (5 × s, 9 H, CH_3Ar).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.44 (HNCOPh), 170.19 (HNCOPh), 166.03 (*C*OCH=C), 164.91 (*C*OCH=C), 164.24 [CH=*C*(Ar)O], 163.94 [CH=*C*(Ar)O], 154.33 (Ar*C*OO), 154.17 (Ar*C*OO), 141.09 (Ar*C*), 136.35 (Ar*C*), 136.24 (Ar*C*), 136.16 (Ar*C*), 136.08 (Ar*C*), 135.68 (Ar*C*), 135.64 (Ar*C*), 134.76 (Ar*C*), 134.53 (Ar*C*), 132.60 (Ar*C*), 132.56 (Ar*C*), 131.71 (Ar*C*), 131.59 (Ar*C*), 131.24 (Ar*C*), 131.04 (Ar*C*), 130.89 (Ar*C*), 130.83 (Ar*C*), 130.76 (Ar*C*), 130.72 (Ar*C*), 129.79 (Ar*C*), 129.66 (Ar*C*), 129.52

(Ar*C*), 129.48 (Ar*C*), 129.16 (Ar*C*), 129.07 (Ar*C*), 128.11 (Ar*C*), 127.92 (Ar*C*), 126.94 (Ar*C*), 126.77 (Ar*C*), 125.85 (Ar*C*), 125.81 (Ar*C*), 125.59 (Ar*C*), 125.45 (Ar*C*), 112.12 (CO*C*H=C), 111.45 (CO*C*H=C), 49.47 [CON(CH$_3$)*C*H$_2$], 46.84 [CON(CH$_3$)*C*H$_2$], 38.29 (*C*H$_2$NHCOPh), 37.99 (*C*H$_2$NHCOPh), 36.67 [CON(*C*H$_3$)CH$_2$], 33.52 [CON(*C*H$_3$)CH$_2$], 21.56 (CH$_3$Ar), 21.50 (CH$_3$Ar), 20.43 (CH$_3$Ar), 20.32 (CH$_3$Ar), 19.89 (CH$_3$Ar), 19.72 (CH$_3$Ar).

(*Z*)-3-{[2-(2-Fluorobenzamido)ethyl](methyl)amino}-1-(2-fluorophenyl)-1-(2-fluorophenylcarbonyloxy)-3-oxoprop-1-ene (14g)

The title compound **14g** was prepared using 1,2-dimethylimidazoline (**11**; 0.098 g, 1 mmol) and 2-fluorobenzoyl chloride (0.555 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–acetone, 4:1→2:1). The ratio of the two rotational conformations was 2.68:1 based on the relative integrals of the 3.23 and 3.01 ppm resonance of the ^{1}H NMR spectrum.

Yield: 173 mg (36%); white solid; mp 91–93 °C; R_f = 0.44 (hexane–acetone, 1:1).

IR (KBr): 3259, 1738, 1651, 1613 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.09–6.97 (m, 13 H, NH and ArH), 6.73 and 6.68 (s, 1 H, COCH=C), 3.75–3.66 (m, 4 H, C*H*$_2$C*H*$_2$), 3.23 and 3.01 (s, 3 H, NCH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 166.89 (d, $^3J_{CF}$ = 3.2 Hz, HNCOPh), 166.68 (d, $^3J_{CF}$ = 3.1 Hz, HNCOPh), 163.97 [d, $^3J_{CF}$ = 2.0 Hz, CH=*C*(Ar)O], 163.75 [d, $^3J_{CF}$ = 2.0 Hz, CH=*C*(Ar)O], 160.48 (d, $^1J_{CF}$ = 249.1 Hz, Ar*C*), 160.02 (d, $^1J_{CF}$ = 252.8 Hz, Ar*C*), 159.49 (d, $^1J_{CF}$ = 251.6 Hz, Ar*C*), 159.35 (d, $^1J_{CF}$ = 252.7 Hz, Ar*C*), 159.30 (d, $^1J_{CF}$ = 252.3 Hz, Ar*C*), 158.85 (d, $^1J_{CF}$ = 250.8 Hz, Ar*C*), 147.43 (d, $^3J_{CF}$ = 3.7 Hz, Ar*C*OO), 146.54 (d, $^3J_{CF}$ = 4.3 Hz, Ar*C*OO), 135.29 (d, $^3J_{CF}$ = 9.1 Hz, Ar*C*), 135.18 (d, $^3J_{CF}$ = 7.4 Hz, Ar*C*), 133.25 (d, $^3J_{CF}$ = 9.2 Hz, Ar*C*), 132.99 (d, $^3J_{CF}$ = 9.1 Hz, Ar*C*), 132.69 (Ar*C*), 132.50 (Ar*C*), 131.61 (d, $^4J_{CF}$ = 1.1 Hz, Ar*C*), 131.51 (d, $^4J_{CF}$ = 2.1 Hz, Ar*C*), 131.31 (d, $^3J_{CF}$ = 8.9 Hz, Ar*C*), 131.25 (d, $^3J_{CF}$ = 9.1 Hz, Ar*C*), 128.56 (d, $^4J_{CF}$ = 1.6 Hz, Ar*C*), 124.56 (d, $^3J_{CF}$ = 3.3 Hz, Ar*C*), 124.42 (d, $^4J_{CF}$ = 2.5 Hz, Ar*C*), 124.38 (d, $^3J_{CF}$ = 3.5 Hz, Ar*C*), 124.33 (d, $^3J_{CF}$ = 3.9 Hz, Ar*C*), 124.15 (d, $^3J_{CF}$ = 3.9 Hz, Ar*C*), 121.73 (d, $^2J_{CF}$ = 10.4 Hz, Ar*C*), 120.71 (d, $^2J_{CF}$ = 11.8 Hz, Ar*C*), 117.53 (d, $^2J_{CF}$ = 9.0 Hz, Ar*C*), 117.28 (d, $^2J_{CF}$ = 9.0 Hz, Ar*C*), 117.01 (d, $^2J_{CF}$ = 22.0 Hz, Ar*C*), 116.97 (d, $^2J_{CF}$ = 22.0 Hz, Ar*C*), 116.42 (d, $^2J_{CF}$ = 22.8 Hz, Ar*C*), 116.39 (d, $^2J_{CF}$ = 22.6 Hz, Ar*C*), 115.98 (d, $^2J_{CF}$ = 24.3 Hz, Ar*C*), 115.92 (d, $^2J_{CF}$ = 24.3 Hz, Ar*C*), 113.98 (d, $^4J_{CF}$ = 11.2 Hz, CO*C*H=C), 113.12 (d, $^4J_{CF}$ = 11.2 Hz, CO*C*H=C), 49.41 [CON(CH$_3$)*C*H$_2$], 46.90 [CON(CH$_3$)*C*H$_2$], 38.57 (*C*H$_2$NHCOPh), 38.52 (*C*H$_2$NHCOPh), 37.00 [CON(*C*H$_3$)CH$_2$], 33.93 [CON(*C*H$_3$)CH$_2$].

(*Z*)-3-{[2-(3-Chlorobenzamido)ethyl](methyl)amino}-1-(3-chlorophenyl)-1-(3-chlorophenylcarbonyloxy)-3-oxoprop-1-ene (14h)

The title compound **14h** was prepared using 1,2-dimethylimidazoline (**11**; 0.098 g, 1 mmol) and 3-chlorobenzoyl chloride (0.613 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–EtOAc, 1:2→EtOAc). The ratio of the two rotational conformations was 2.16:1 based on the relative integrals of the 3.23 and 2.93 ppm resonances of the ^{1}H NMR spectrum.

Yield: 276 mg (52%); white solid; mp 94–96 °C; R_f = 0.43 (EtOAc).

IR (KBr): 3317, 1738, 1651, 1602 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.11–7.14 (m, 13 H, NH and ArH), 6.63 and 6.55 (2 × s, 1 H, COCH=C), 3.74–3.59 (m, 4 H, C*H*$_2$C*H*$_2$), 3.23 and 2.93 (2 × s, 3 H, NCH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 166.56 (HN*C*OPh), 166.19 (HN*C*OPh), 165.84 (*C*OCH=C), 164.36 (*C*OCH=C), 162.97 [CH=*C*(Ar)O], 162.43 (CH=*C*(Ar)O], 152.59 (Ar*C*OO), 151.71 (Ar*C*OO), 135.25 (Ar*C*), 135.15 (Ar*C*), 134.98 (Ar*C*), 134.92 (Ar*C*), 134.82 (Ar*C*), 134.70 (Ar*C*), 134.64 (Ar*C*), 134.37 (Ar*C*), 134.17 (Ar*C*), 133.84 (Ar*C*), 133.75 (Ar*C*), 131.41 (Ar*C*), 131.12 (Ar*C*), 130.41 (Ar*C*), 130.33 (Ar*C*), 130.23 (Ar*C*), 130.10 (Ar*C*), 130.05 (Ar*C*), 129.99 (Ar*C*), 129.90 (Ar*C*), 129.87 (Ar*C*), 129.46 (Ar*C*), 129.41 (Ar*C*), 128.29 (Ar*C*), 128.08 (Ar*C*), 127.44 (Ar*C*), 125.52 (Ar*C*), 125.40 (Ar*C*), 125.27 (Ar*C*), 124.56 (Ar*C*), 123.63 (Ar*C*), 123.38 (Ar*C*), 109.17 (CO*C*H=C), 107.38 (CO*C*H=C), 49.35 [CON(CH$_3$)*C*H$_2$], 47.07 [CON(CH$_3$)*C*H$_2$], 39.11 (*C*H$_2$NHCOPh), 38.27 (*C*H$_2$NHCOPh), 36.78 [CON(*C*H$_3$)CH$_2$], 33.53 [CON(*C*H$_3$)CH$_2$].

(*Z*)-3-{[2-(3-Methylbenzamido)ethyl](methyl)amino}-1-(3-methylphenyl)-1-(3-methylphenylcarbonyloxy)-3-oxoprop-1-ene (14i)

The title compound **14i** was prepared using 1,2-dimethylimidazoline (**11**; 0.098 g, 1 mmol) and 3-methylbenzoyl chloride (0.541 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–acetone, 4:1→2:1). The ratio of the two rotational conformations was 2.35:1 based on the relative integrals of the 3.21 and 2.89 ppm resonances of the ^{1}H NMR spectrum.

Yield: 282 mg (65%); white solid; mp 118–120 °C; R_f = 0.56 (hexane–acetone, 1:1).

IR (KBr): 3319, 1729, 1650, 1615 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.97–7.10 (m, 13 H, NH and ArH), 6.60 and 6.51 (2 × s, 1 H, COCH=C), 3.72–3.58 (m, 4 H, C*H*$_2$C*H*$_2$), 3.21 and 2.89 (2 × s, 3 H, NCH$_3$), 2.39, 2.35, 2.32, 2.29 and 2.26 (5 × s, 9 H, CH$_3$Ar).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 168.16 (HNCOPh), 167.48 (HNCOPh), 166.75 (*C*OCH=C), 164.98 (*C*OCH=C), 164.42 [CH=*C*(Ar)O], 164.13 [CH=*C*(Ar)O], 153.71 (Ar*C*OO), 153.01 (Ar*C*OO), 138.46 (Ar*C*), 138.40 (Ar*C*), 138.23 (Ar*C*), 138.01 (Ar*C*), 137.91 (Ar*C*), 134.54 (Ar*C*), 134.49 (Ar*C*), 133.68 (Ar*C*), 133.66 (Ar*C*), 133.55 (Ar*C*), 132.05 (Ar*C*), 131.83 (Ar*C*), 131.01 (Ar*C*), 130.87 (Ar*C*), 130.77 (Ar*C*), 130.60 (Ar*C*), 129.06 (Ar*C*), 128.67 (Ar*C*), 128.63 (Ar*C*), 128.50 (Ar*C*), 128.46 (Ar*C*), 128.16 (Ar*C*), 128.04 (Ar*C*), 127.88 (Ar*C*), 127.79 (Ar*C*), 127.48 (Ar*C*), 127.23 (Ar*C*), 126.09 (Ar*C*), 126.00 (Ar*C*), 124.20 (Ar*C*), 123.69 (Ar*C*), 122.74 (Ar*C*), 122.67 (Ar*C*), 108.27 (CO*C*H=C), 106.75 (CO*C*H=C), 49.61 [CON(CH$_3$)*C*H$_2$], 47.21 [CON(CH$_3$)*C*H$_2$], 39.11 (*C*H$_2$NHCOPh), 38.49 (*C*H$_2$NHCOPh), 37.11 [CON(*C*H$_3$)CH$_2$], 33.92 [CON(*C*H$_3$)CH$_2$], 21.41 (CH$_3$Ar), 21.35 (CH$_3$Ar), 21.28 (CH$_3$Ar), 21.21 (CH$_3$Ar), 21.19 (CH$_3$Ar).

HRMS: *m*/*z* [M]$^+$ calcd for $C_{29}H_{30}N_2O_4$: 470.2206; found: 470.2201.

(*Z*)-3-{[2-(3-Methoxybenzamido)ethyl](methyl)amino}-1-(3-methoxyphenyl)-1-(3-methoxyphenylcarbonyloxy)-3-oxoprop-1-ene (14j)

The title compound **14j** was prepared using 1,2-dimethylimidazoline (**11**; 0.098 g, 1 mmol) and 3-methoxybenzoyl chloride (0.597 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–acetone, 3:1→1:1). The ratio of the two rotational conformations was 2.91:1 based on the relative integrals of the 3.21 and 2.91 ppm resonances of the ^{1}H NMR spectrum.

Yield: 284 mg (63%); white solid; mp 100–102 °C; R_f = 0.31 (hexane–actone, 1:1).

IR (KBr): 3320, 1731, 1643, 1619 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76–6.86 (m, 13 H, NH and ArH), 6.64 and 6.52 (2 × s, 1 H, COC*H*=C), 3.83, 3.79, 3.77, 3.75 and 3.72 (5 × s, 9 H, CH_3OC), 3.62 (m, 4 H, CH_2CH_2), 3.21 and 2.91 (2 × s, 3 H, NCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.96 (HNCOAr), 167.04 (HNCOAr), 166.84 (*C*OCH=C), 164.85 (*C*OCH=C), 164.09 [CH=*C*(Ar)O], 163.79 [CH=*C*(Ar)O], 161.05 (CH_3O*C*), 159.74 (CH_3O*C*), 159.61 (CH_3O*C*), 159.54 (CH_3O*C*), 159.47 (CH_3O*C*), 159.40 (CH_3O*C*), 153.30 (Ar*C*OO), 152.48 (Ar*C*OO), 135.20 (Ar*C*), 135.06 (Ar*C*), 130.27 (Ar*C*), 129.85 (Ar*C*), 129.78 (Ar*C*), 129.63 (Ar*C*), 129.28 (Ar*C*), 129.16 (Ar*C*), 128.97 (Ar*C*), 122.76 (Ar*C*), 122.43 (Ar*C*), 120.56 (Ar*C*), 120.37 (Ar*C*), 119.09 (Ar*C*), 118.73 (Ar*C*), 117.98 (Ar*C*), 117.93 (Ar*C*), 117.86 (Ar*C*), 115.58 (Ar*C*), 115.37 (Ar*C*), 115.36 (Ar*C*), 114.56 (Ar*C*), 114.14 (Ar*C*), 112.08 (Ar*C*), 111.87 (Ar*C*), 111.57 (Ar*C*), 111.48 (Ar*C*), 108.89 (CO*C*H=C), 107.18 (CO*C*H=C), 55.41 (CH_3OC), 55.31 (CH_3OC), 55.28 (CH_3OC), 55.23 (CH_3OC), 55.15 (CH_3OC), 49.63 [$CON(CH_3)CH_2$], 47.24 [$CON(CH_3)CH_2$], 39.31 ($CH_2NHCOAr$), 38.59 ($CH_2NHCOAr$), 37.09 [$CON(CH_3)CH_2$], 33.87 [$CON(CH_3)CH_2$].

HRMS: *m/z* $[M]^+$ calcd for $C_{29}H_{30}N_2O_7$: 518.2053; found: 518.2067.

(*Z*)-3-{[2-(3-Fluorobenzamido)ethyl](methyl)amino}-1-(3-fluorophenyl)-1-(3-fluorophenylcarbonyloxy)-3-oxoprop-1-ene (14k)

The title compound **14k** was prepared using 1,2-dimethylimidazoline (**11**; 0.098 g, 1 mmol) and 3-fluorobenzoyl chloride (0.555 g, 3.5 mmol) by the general procedure, and purified by flash column chromatography (silica gel; hexane–acetone, 4:1→2:1). The ratio of the two rotational conformations was 2.36:1 based on the relative integrals of the 3.23 and 2.89 ppm resonances of the ^{1}H NMR spectrum.

Yield: 207 mg (43%); white solid; mp 154–156 °C; R_f = 0.44 (hexane–acetone, 1:1).

IR (KBr): 3325, 1747, 1656, 1614 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.94–7.06 (m, 13 H, NH and ArH), 6.64 and 6.57 (2 × s, 1 H, COC*H*=C), 3.73–3.57 (m, 4 H, CH_2CH_2), 3.23 and 2.89 (2 × s, 3 H, NCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.66 (d, $^4J_{CF}$ = 2.5 Hz, HN*C*O-Ph), 166.25 (*C*OCH=C), 165.85 (d, $^4J_{CF}$ = 2.5 Hz, HN*C*OPh), 164.28 (*C*OCH=C), 163.04 (d, $^4J_{CF}$ = 3.1 Hz, COCH=*C*), 162.74 (d, $^1J_{CF}$ = 247.0 Hz, Ar*C*), 162.65 (d, $^1J_{CF}$ = 245.5 Hz, Ar*C*), 162.53 (d, $^4J_{CF}$ = 3.1 Hz, COCH=*C*), 162.45 (d, $^1J_{CF}$ = 246.9 Hz, Ar*C*), 162.39 (d, $^1J_{CF}$ = 247.7 Hz, Ar*C*), 162.33 (d, $^1J_{CF}$ = 248.2 Hz, Ar*C*), 162.30 (d, $^1J_{CF}$ = 246.9 Hz, Ar*C*), 152.55 (d, $^4J_{CF}$ = 2.8 Hz, Ar*C*OO), 151.75 (d, $^4J_{CF}$ = 2.9 Hz, Ar*C*OO), 135.89 (d, $^3J_{CF}$ = 6.8 Hz, Ar*C*), 135.68 (d, $^3J_{CF}$ = 6.4 Hz, Ar*C*), 135.59 (d, $^3J_{CF}$ = 7.7 Hz, Ar*C*), 135.48 (d, $^3J_{CF}$ = 8.1 Hz, Ar*C*), 130.83 (d, $^3J_{CF}$ = 7.6 Hz, Ar*C*), 130.45 (d, $^3J_{CF}$ = 8.5 Hz, Ar*C*), 130.42 (d, $^3J_{CF}$ = 7.8 Hz, Ar*C*), 130.32 (d, $^3J_{CF}$ = 8.1 Hz, Ar*C*), 130.27 (d, $^3J_{CF}$ = 7.7 Hz, Ar*C*), 130.25 (d, $^3J_{CF}$ = 8.2 Hz, Ar*C*), 129.80 (d, $^3J_{CF}$ = 7.8 Hz, Ar*C*), 129.73 (d, $^3J_{CF}$ = 7.7 Hz, Ar*C*), 125.92 (d, $^4J_{CF}$ = 3.1 Hz, Ar*C*), 125.75 (d, $^4J_{CF}$ = 3.0 Hz, Ar*C*), 122.86 (d, $^4J_{CF}$ = 2.9 Hz, Ar*C*), 122.19 (d, $^4J_{CF}$ = 2.9 Hz, Ar*C*), 121.15 (d, $^4J_{CF}$ = 3.1 Hz, Ar*C*), 120.98 (d, $^2J_{CF}$ = 22.6 Hz, Ar*C*), 120.95 (d, $^4J_{CF}$ = 2.9 Hz, Ar*C*), 120.86 (d, $^2J_{CF}$ = 21.1 Hz, Ar*C*), 118.34 (d, $^2J_{CF}$ = 22.2 Hz, Ar*C*), 118.06 (d, $^2J_{CF}$ = 21.5 Hz, Ar*C*), 117.27 (d, $^2J_{CF}$ = 21.1 Hz, Ar*C*), 117.10 (d, $^2J_{CF}$ = 22.5 Hz, Ar*C*), 116.99 (d, $^2J_{CF}$ = 22.0 Hz, Ar*C*), 116.80 (d, $^2J_{CF}$ = 23.4 Hz, Ar*C*), 114.37 (d, $^2J_{CF}$ = 23.0 Hz, Ar*C*), 114.19 (d, $^2J_{CF}$ = 22.9 Hz, Ar*C*), 112.50 (d, $^2J_{CF}$ = 23.6 Hz, Ar*C*), 112.31 (d, $^2J_{CF}$ = 23.6 Hz, Ar*C*), 109.08 (CO*C*H=C), 107.62 (CO*C*H=C), 49.26 [$CON(CH_3)CH_2$], 47.08 [$CON(CH_3)CH_2$], 39.22 ($CH_2NHCOPh$), 38.26 ($CH_2NHCOPh$), 36.79 [$CON(CH_3)CH_2$], 33.41 [$CON(CH_3)CH_2$].

HRMS: *m/z* $[M]^+$ calcd for $C_{26}H_{21}F_3N_2O_4$: 482.1453; found: 482.1459.

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(29) X-ray crystallographic description of **12a**: Crystal dimensions (mm): $0.38 \times 0.35 \times 0.22$. $C_{26}H_{25.5}N_2O_{4.25}$; Mr = 433.98. Triclinic; space group $P\bar{1}$; a = 8.571(2) Å, b = 10.140(2) Å, c = 14.383(3) Å; α = 103.687(3)°, β = 106.909(3)°, γ = 96.759(4)°; V = 1138.5(4) Å^3; Z = 2; D(calcd) = 1.266 g/cm^3; μ (mm^{-1}) = 0.086; F(000) = 459; Reflections collected/unique = 8421/4000; refinement method: full-matrix least-squares on F^2; final R indices [$I > 2\sigma(I)$]. $R1$ = 0.0468, $wR2$ = 0.1099, R indices (all data) $R1$ = 0.1093, $wR2$ = 0.1370; goodness of fit on F^2 = 1.000. Crystals were grown by slow evaporation of pentane into a $CHCl_3$–EtOAc solution of **12a**. CCDC number for compound **12a** is CCDC 683239. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via ww.ccdc.cam.ac.uk/datarequest/cif.

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