AN EFFICIENT SYNTHESIS OF 1-(*o*-VINYLENEBENZYL)-BENZIMIDAZOLIN-2-ONES

Sung Cheol Yoon and Kyongtae Kim*

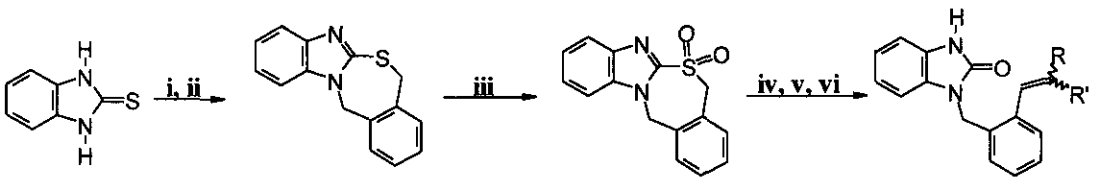
Department of Chemistry, Seoul National University, Seoul 151-742, Korea

Abstract - 5*H*,13*H*-Benzo[5,6][1,3]thiazepino[4,3-*a*]benzimidazole (**2**), prepared by the reaction of benzimidazoline-2-thione with α,α'-dibromo-*o*-xylene in the presence of sodium hydride in tetrahydrofuran, was oxidized by *m*-chloroperbenzoic acid to give the corresponding sulfone which was treated with *n*-butyllithium at -78 °C, followed by addition of aldehydes to give the title compounds in excellent yields.

Synthesis of 1-substituted benzimidazolin-2-ones has recently attracted much attention owing to their various biological activities such as antiulcer,[1,2] neureoleptic,[3] antihistaminic,[4] antihypertensive,[5] and antiallergic[6] activities. Numerous methods for the synthesis of 1-substituted benzimidazolin-2-ones without concomitant formations of 1,3-disubstituted benzimidazolin-2-ones have been reported: One of the methods involves heating of *o*-phenylenediamine with β-keto esters in xylene to give 1-vinylenebenzimidazolin-2-ones.[7-9] Treatment of *ortho* diisocyanate which is prepared by thermal degradation of the polymer obtained by allowing the *o*-arylenediamine to react with excess phosgene, with aniline or methanol gave 1-(*N*-phenylcarbonyl)- and 1-carbomethoxybenzimidazolin-2-ones, respectively.[10] Thermolysis of suitably substituted aroyl azides in xylene led to either 1-alkyl or 1-benzoylbenzimidazolin-2-ones in relatively high yields.[11,12] *N*-Monoalkylation of benzimidazolin-2-ones was also achieved by alkylation at *N*-3 of 1-isopropylidenebenzimidazolin-2-one in DMF in the presence of NaH, followed by hydrolysis with cold aqueous sulfuric acid.[13,14] However, all of these reactions are of limited use and appears to be tedious. Thus the development of more efficient methods is still needed.

Previously we reported a facile one step synthesis of 1-alkylbenzimidazoline-2-thiones, which involved the reactions of benzimidazoline-2-thione (**1**) with alkyl halides in the presence of sodium naphthalenide in THF at room temperature under a nitrogen atmosphere and the desired compounds were obtained by *in situ* treatment of the reaction mixture with an additional amount of sodium naphthalenide.[15] In order to prepare 1-benzylbenzimidazoline-2-thione having a variable substituent at *ortho* position of the phenyl ring of the benzyl group, 5*H*,13*H*-Benzo[5,6][1,3]thiazepino[4,3-*a*]benzimidazole (**2**) was prepared by treatment of **1** with NaH at 25 °C, followed by addition of α,α'-dibromo-*o*-xylene according to the literature procedures.[15] Since treatment of **2** with sodium naphthalenide under the same condition as described for the one step synthesis of 1-alkylbenzimidazoline-2-thiones was expected to give 1-(2-methylbenzyl)benzimidazoline-2-thione in view of the result obtained from the reaction of 2,3,4,5-tetrahydro-1,3-thiazepino[3,2-

a]benzimidazole, functionalization at the benzylic carbon α to the sulfur atom of **2** was attempted by treatment of **2** with *n*-BuLi in THF at -78 °C, followed by addition of CH_3I. However, the reaction gave a complex mixture. So compound **2** was oxidized by *m*-chloroperbenzoic acid in ether at room temperature for 2 days to give a sulfone (**3**) in 93 % yield.



1 **2** **3** **4**

Reagents and conditions: **i**, NaH, THF, 25 °C. **ii**, α,α'-dibromo-*o*-xylene, 25 °C, 2 days. **iii**, MCPBA, Et_2O, 25 °C, 2 days. **iv**, *n*-BuLi, THF, -78 °C, 10 min. **v**, RR'C=O, 25 °C, 3 h. **vi**, H_2O.

The sulfone (**3**) was treated with *n*-BuLi at -78 °C, followed by addition of either aliphatic or aromatic aldehydes. The mixture was stirred for 3 h, followed by addition of water at room temperature. Chromatographic separation of the mixture on silica gel (70-230 mesh, Merck) afforded 1-(*o*-vinylenebenzyl)benzimidazolin-2-ones (**4**) in excellent yields. The yields of **4** are summarized in Table 1.

Table 1. Yields of 1-(*o*-vinylenebenzyl)benzimidazolin-2-ones (**4**).

Compound	R'	R	Yield (%)	Compound	R'	R	Yield (%)
4a	H	C_6H_5	99	**4h**	H	*p*-BrC_6H_4	99
4b	H	*o*-$MeOC_6H_4$	99	**4i**	H	$C_6H_5CH_2$	91
4c	H	*o*-MeC_6H_4	99	**4j**	H	Me	93
4d	H	*o*-ClC_6H_4	99	**4k**	H	*n*-Pr	93
4e	H	*o*-$CF_3C_6H_4$	99	**4l**	- $(CH_2)_5$ -		91
4f	H	*m*-MeC_6H_4	99	**4m**	Et	C_6H_5	14[†]
4g	H	*m*-BrC_6H_4	92				

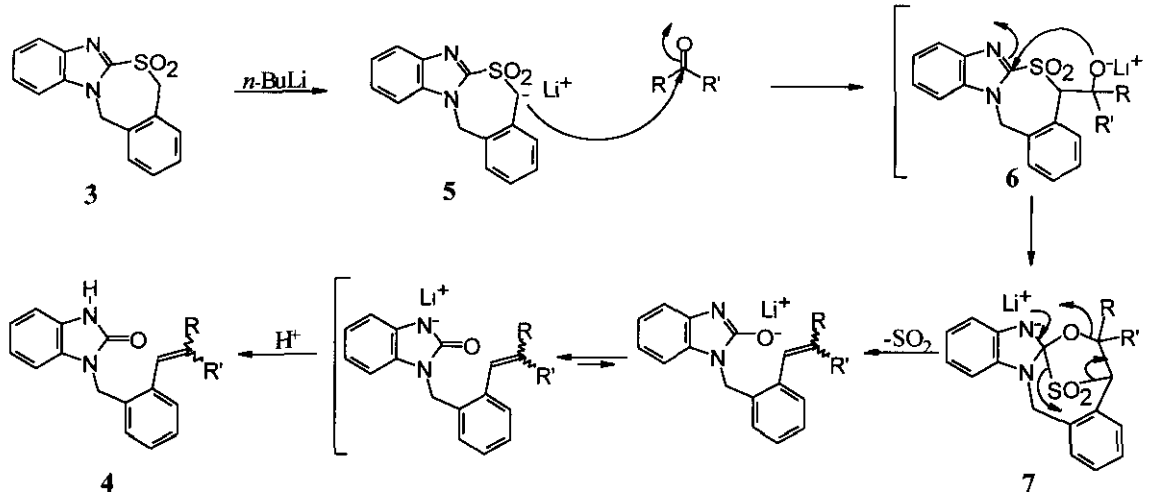
[†]Yield based on ^1H nmr analysis. For the recrystallization were used ethanol (**4a-4i**) and a mixture of CH_2Cl_2 and *n*-hexane (**4j-4m**).

The structures of **4** were determined based on the spectroscopic and mass spectral data and elemental analyses. Of the compounds (**4**), **4a-4i** were assigned to be *trans*-isomers by comparison of their ^1H nmr spectra showing multiplets beginning from the range of δ 6.82 and 7.01, which were arisen from two vinylic and aromatic protons of each compound with the chemical shifts of vinylic protons of *trans*- (δ 7.03) and *cis*-stilbene (δ 6.53).[16] Ir (KBr) spectra of compounds (**4**) showed a strong peak between 970 and 990 cm^{-1} which was a characteristic band for *trans*-isomers.[17]

On the other hand, 1-[2-(1-propenyl)benzyl]benzimidazolin-2-one (**4j**) showed two double doublets at δ 1.67 (J = 7.1, 1.7 Hz) and 1.91 (J = 6.6, 1.5 Hz) due to methyl protons coupled with two vinylic protons of *cis*- and *trans*-isomers and two singlets (1:1) at δ 5.07 and 5.15 due to benzylic protons of *cis*- and *trans*-**4j**. The signal of a vinylic proton at C-β of *o*-propenyl group of **4j**, appeared at δ 5.92 (J = 11.3, 7.0 Hz) and 6.10 (J= 15.5, 6.6 Hz) as two overlapped quartets which were arisen from the coupling between a proton at C-α and a methyl protons of *o*-propenyl group. This result was in good agreement with ^{1}H nmr spectral data of *cis-o*-propenyltoluene[18] in which the signal of the vinyl proton at C-β appeared at δ 5.74 with coupling constants, J = 11.5 and 7.0 Hz whereas that of *trans*-isomer appeared at δ 5.97 with J = 15.5, 6.5 Hz. Accordingly the signals at δ 5.92 and 6.10 were assigned to the protons at C-β of *cis*- and *trans*-**4j**, respectively. In addition, *cis-o*-propenyltoluene showed the ^{1}H nmr signals at δ 2.21 and 1.74, which were due to the methyl group bonded to the phenyl ring and the methyl group at C-β of the propenyl group, respectively whereas the corresponding ^{1}H nmr signals of *trans*-isomer appeared at δ 2.27 and 1.87. Therefore, double doublets at δ 1.67 and 1.91, and a singlet at δ 5.07 and 5.15 were assigned to a methyl and a benzylic protons of *cis*- and *trans*-**4j**, respectively. In the meantime, ir (KBr) spectrum of **4j** showed a band at 975 and 690 cm^{-1} which corresponded to alkene C-H bending vibrations of *trans*- and *cis*-**4j**, respectively.

Apart from the aldehydes, similar treatments of ketones underwent the reactions in different manner. That is, the reactions of propiophenone afforded **4m** in 14% yield along with other unidentifiable mixtures. The reaction of acetone gave a complex mixture. However, cyclohexanone afforded the expected compound (**4l**) in 91% yield.

The mechanism of the formation of **4** from **3** is proposed as the following:



Treatment of **3** with *n*-BuLi generates readily a benzylic carbanion (**5**) which is also stabilized by a sulfonyl group. Nucleophilic attack of the carbanion to the carbonyl carbon of an aldehyde generates an alkoxy anion (**6**), which attacks intramolecularly the imino carbon of the benzimidazole ring to form **7**, which is then converted to **4** *via* a ring-opening by extrusion of SO_2, followed by protonation. Analogous mechanism has

been proposed for the formation of alkenes from the reactions of alkyl benzothiazolyl sulfone with LDA, *followed by treatment of ketones.*[19]

EXPERIMENTAL

Benzimidazoline-2-thione, α,α'-dibromo-*o*-xylene, *m*-chloroperbenzoic acid, and all carbonyl compounds were obtained from Aldrich Chemical Co., Inc.. 5*H*,13*H*-Benzo[5,6][1,3]thiazepino[4,3-*a*]benzimidazole (**2**) was prepared by the literature method.[15] THF from Merck was freshly distilled from sodium prior to use. And all of other solvents were obtained from Duksan Pharm. Co. Ltd. Thin layer chromatography was carried out on Merck Chromatogram sheet (Kiesel gel 60 F_{254}). The chromatogram was visuallized by a mineral ultraviolet lamp. Column chromatography was performed using silica gel (Merck, 70-230 mesh). ^{1}H Nmr spectra were obtained with a Varian EM-360A at 60 MHz, a Bruker AC-80 at 80 MHz, or a Bruker AW-200 at 200 MHz, using tetramethylsilane as an internal standard. Infrared (ir) spectra were obtained using a Perkin-Elmer Model 782 or a Shimazu infrared spectrophotometer. Mass spectra (ms) were obtained by a VG 12-250 mass spectrometer at 70 eV. Melting points were determined on a Fisher-Johns melting point apparatus and were uncorrected.

5*H*,13*H*-Benzo[5,6][1,3]thiazepino[4,3-*a*]benzimidazole-6,6-dioxide (3). (i) Oxidation of **2** with MCPBA: To a solution of **2** (181 mg, 0.717 mmol) in dried MeCN (20 ml) was dropwisely added MCPBA (374 mg) in dried Et_2O (10 ml) for 30 min. The reaction mixture was stirred at room temperature for 2 days. After the solvent was removed *in vacuo*, the residue was neutralized with saturated $NaHCO_3$, followed by extraction with EtOAc (100 ml x 2). The combined EtOAc extracts were dried over $MgSO_4$ and evaporated to dryness. The residue was chromatographed on a silica gel column (2 x 12 cm). Elution with a mixture of *n*-hexane and EtOAc (1:2, 150 ml) gave **3** (190 mg, 93%): mp 209.5-210.5 °C (from EtOH): Ir (KBr) (υ, cm^{-1}) 2925, 1600, 1460, 1440, 1320(s), 1160, 1148, 1127, 823, 750; ^{1}H nmr (60 MHz, DMSO-d_6, δ, ppm) 5.19 (2H, s, N-CH_2), 5.52 (2H, s, SO_2CH_2), 7.01-7.75 (8H, m, ArH); Anal. Calcd for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.25; N, 9.85; S, 11.28. Found: C, 63.30; H, 4.29; N, 9.90; S, 11.19. (ii) Oxidation of **2** with OXONE®: To a solution of **2** (817 mg, 3.24 mmol) in MeOH (20 ml) at 0°C was added a solution of OXONE® (5.971 g, 9.71 mmol) in water (10 ml), which was stirred for 30 min. The resulting cloudy slurry was stirred for an additional 5h at room temperature. The mixture was diluted with water (200 ml), followed by extraction with EtOAc (200 ml). The combined organic layers were washed with water and then with brine. Drying of the organic layers over $MgSO_4$, followed by evaporation of the solvent *in vacuo* gave **3** (873 mg, 95%) as white solids.

General Procedure for Synthesis of 1-(*o*-Vinylenebenzyl)benzimidazolin-2-ones (4). To a solution of **3** (56-151 mg, 0.197-0.528 mmol) in dried THF (10 ml) was added with *n*-BuLi (2.5 M in hexane, 2.5 equiv.) at -78 °C under a nitrogen atmosphere, followed by dropwise addition of benzaldehydes (5 equiv.) for 30 min. The mixture was stirred at room temperature for 3 h and then quenched by water (10 ml). After THF was

removed *in vacuo*, the residue was extracted with EtOAc (150 ml) and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on a silica gel column (2 x 10 cm). A small amount of benzaldehyde was removed by elution with CH_2Cl_2. Elution next with a mixture of *n*-hexane and EtOAc (2:1, 60 ml) gave **4** as white solids. Ethanol was used for the crystallization of **4a-4i** and a mixture of CH_2Cl_2 and *n*-hexane for **4j-4m**.

1-[*trans*-2-(2-Phenylvinyl)benzyl]benzimidazolin-2-one (4a): Compound (**3**) (56 mg, 0.197 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of benzaldehyde (114 mg, 1.07 mmol) in dried THF (10 ml). Chromatography of the residue gave **4a** (63 mg, 99%): mp 205.5-207 °C (from EtOH): Ir (KBr) (υ, cm^{-1}) 3125, 3050, 2965-2600, 1700, 1620, 1484, 1398, 1149, 987 (*trans*), 816, 802, 790, 742; ^1H nmr (60 MHz, DMSO-d_6, δ, ppm) 5.26 (2H, s, N-CH_2), 6.67-8.08 (14H, m, ArH and Ar-CH=CH-Ar (*trans*)), 11.08 (1H, s, Ar-NH-); ms (m/z) 326 (M^+, 14.6), 192 (100), 178 (36.7), 134 (8.3). Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58. Found: C, 80.89; H, 5.63; N, 8.62.

1-{2-[*trans*-(2-Methoxyphenyl)vinyl]benzyl}benzimidazolin-2-one (4b): Compound (**3**) (97 mg, 0.341 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of *o*-anisaldehyde (232 mg, 1.71 mmol) in dried THF (10 ml). Chromatography of the residue gave **4b** (119 mg, 99%): mp 195-196.5 °C (from EtOH): Ir (KBr) (υ, cm^{-1}) 3125, 3070, 3400-2600, 1720, 1710, 1695, 1680, 1620, 1600, 1495, 1484, 1400, 1250, 1030, 985 (*trans*), 755, 735, 692; ^1H nmr (60 MHz, DMSO-d_6, δ, ppm) 3.91 (3H, s, OCH_3), 5.27 (2H, s, N-CH_2), 6.85-8.01 (14H, m, ArH and Ar-CH=CH-Ar (*trans*)), 10.92 (1H, s, Ar-NH-); ms (m/z) 356 (M^+, 14.9), 223 (71.3), 207 (34.6), 192 (9.3), 178 (34.8), 134 (9.4). Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86. Found: C, 77.48; H, 5.63; N, 7.89.

1-{2-[*trans*-(2-Methylphenyl)vinyl]benzyl}benzimidazolin-2-one (4c): Compound (**3**) (112 mg, 0.393 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of *o*-tolualdehyde (236 mg, 1.97 mmol) in dried THF (10 ml). Chromatography of the residue gave **4c** (83 mg, 99%): mp 205.5-207 °C (from EtOH): Ir (KBr) (υ, cm^{-1}) 3125, 3050, 2965-2600, 1700, 1690, 1487, 1400, 1148, 978 (*trans*), 780, 752, 739, 623; ^1H nmr (60 MHz, DMSO-d_6, δ, ppm) 2.41 (3H, s, CH_3), 5.18 (2H, s, N-CH_2), 6.67-7.97 (14H, m, ArH and Ar-CH=CH-Ar (*trans*)), 10.58 (1H, s, Ar-NH-); ms (m/z) 356 (M^+, 14.9), 223 (71.3), 207 (34.6), 192 (9.3), 178 (34.8), 134 (9.4). Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.20; H, 5.94; N, 8.23. Elution next with a mixture of *n*-hexane and EtOAc (1:1, 50 ml) gave **3** (42 mg, 38%).

1-{2-[*trans*-(2-Chlorophenyl)vinyl]benzyl}benzimidazolin-2-one (4d): Compound (**3**) (95 mg, 0.334 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of *o*-chlorobenzaldehyde (235 mg, 1.67 mmol) in dried THF (10 ml). Chromatography of the residue gave **4d** (120 mg, 99%): mp 202-204.5 °C (from EtOH): Ir (KBr) (υ, cm^{-1}) 3140, 3070, 2965-2600, 1710, 1692, 1670, 1620, 1487, 1400, 1145, 1038, 972 (*trans*), 765, 740; ^1H nmr (60 MHz, DMSO-d_6, δ, ppm) 5.27 (2H, s, N-CH_2), 6.82-8.12 (14H, m, ArH and Ar-CH=CH-Ar (*trans*)), 10.97 (1H, s, Ar-NH-); ms (m/z) 362 (M+2, 1.7), 360 (M^+, 3.8), 226 (100), 192

(85.9), 178 (6.2), 134 (17.5). Anal. Calcd for $C_{22}H_{17}N_2OCl$: C, 73.23; H, 4.75; N, 7.76. Found: C, 73.19; H, 4.72; N, 7.79.

1-{2-[*trans*-(2-Trifluoromethylphenyl)vinyl]benzyl}benzimidazolin-2-one (4e): Compound (**3**) (80 mg, 0.282 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of *o*-trifluoromethylbenzaldehyde (125 mg, 1.04 mmol) in dried THF (10 ml). Chromatography of the residue gave **4e** (109 mg, 99%): Ir (KBr) (υ, cm^{-1}) 3650-2600, 3150, 3060, 1705, 1690, 1675, 1480, 1395, 1312, 1158, 1120, 1035, 970 (*trans*), 760, 750, 732, 690; ^1H nmr (60 MHz, DMSO-d_6, δ, ppm) 5.33 (2H, s, N-CH_2-), 6.79-8.58 (14H, m, ArH and Ar-CH=CH-Ar (*trans*)), 11.23 (1H, s, Ar-NH-); ms (m/z) 394 (M^+, 15.4), 260 (100), 192 (22.6), 178 (6.3), 134 (34.6). Anal. Calcd for $C_{23}H_{17}N_2O\,F_3$: C, 70.04; H, 4.34; N, 7.10. Found: C, 70.07; H, 4.35; N, 7.08.

1-{2-[*trans*-(3-Methylphenyl)vinyl]benzyl}benzimidazolin-2-one (4f): Compound (**3**) (59 mg, 0.208 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of *m*-tolualdehyde (125 mg, 1.04 mmol) in dried THF (10 ml). Chromatography of the residue gave **4f** (70 mg, 99%): mp 162-164 °C (from EtOH): Ir (KBr) (υ, cm^{-1}) 3125, 3050, 2965-2600, 1700, 1690, 1487, 1400, 1148, 976 (*trans*), 780, 752, 739; ^1H nmr (60 MHz, DMSO-d_6, δ, ppm) 2.35 (3H, s, CH_3), 5.27 (2H, s, N-CH_2), 6.82-7.65 (14H, m, ArH and Ar-CH=CH-Ar (*trans*)), 9.74 (1H, s, Ar-NH-); ms (m/z) 340 (M^+, 18.7), 206 (100), 192 (28.1), 178 (12.3), 134 (8.2). Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.19; H, 5.95; N, 8.21.

1-{2-[*trans*-(3-Bromophenyl)vinyl]benzyl}benzimidazolin-2-one (4g): Compound (**3**) (151 mg, 0.528 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of *m*-bromobenzaldehyde (308 mg, 2.64 mmol) in dried THF (10 ml). Chromatography of the residue gave **4g** (197 mg, 92%): mp 206-208 °C (from EtOH): Ir (KBr) (υ, cm^{-1}) 3650-2600, 3150, 3060, 1705, 1690, 1675, 1480, 1395, 1312, 1158, 1120, 1035, 970 (*trans*), 760, 750, 732, 690; ^1H nmr (60 MHz, DMSO-d_6, δ, ppm) 5.33 (2H, s, N-CH_2,), 6.79-8.58 (14H, m, ArH and Ar-CH=CH-Ar (*trans*)), 11.23 (1H, s, Ar-NH-); ms (m/z) 407 (M^+, 2.8), 405 (2.7), 272 (45.0), 270 (43.2), 192 (91.3), 178 (4.7), 134 (21.9). Anal. Calcd for $C_{22}H_{17}N_2OBr$: C, 65.20; H, 4.23; N, 6.91. Found: C, 65.23; H, 4.27; N, 6.84.

1-{2-[*trans*-(4-Bromophenyl)vinyl]benzyl}benzimidazolin-2-one (4h): Compound (**3**) (97 mg, 0.341 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of *p*-bromobenzaldehyde (240 mg, 1.71 mmol) in dried THF (10 ml). Chromatography of the residue gave **4h** (135 mg, 99%): mp 228-230 °C (from EtOH): Ir (KBr) (υ, cm^{-1}) 3450-2600, 3150, 3060, 1701, 1690, 1488, 1400, 1340, 1140, 1020, 970 (*trans*), 818, 753, 732, 690; ^1H nmr (60 MHz, DMSO-d_6, δ, ppm) 5.37 (2H, s, N-CH_2), 6.93-8.26 (14H, m, ArH and Ar-CH=CH-Ar (*trans*)), 11.25 (1H, s, Ar-NH-); ms (m/z) 407 (M+2, 4.3), 405 (M^+, 4.5), 272 (41.9), 270 (42.6), 192 (90.7), 178 (3.9), 134 (19.8). Anal. Calcd for $C_{22}H_{17}N_2OBr$: C, 65.20; H, 4.23; N, 6.91. Found: C, 65.21; H, 4.25; N, 6.88.

1-[*trans*-2-(3-Phenyl-1-propenyl)benzyl]benzimidazolin-2-one (4i): Compound (**3**) (112 mg, 0.392 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of phenylacetaldehyde (235 mg, 0.745 mmol) in

dried THF (10 ml). Chromatography of the residue gave **4i** (121 mg, 91%): mp 138-140 °C (from EtOH): Ir (KBr) (υ, cm^{-1}) 3650-2600, 3150, 3060, 1672, 1652, 1486, 1141, 1005, 973 (*trans*), 888, 734, 606, 560; ^1H nmr (60 MHz, DMSO-d_6, δ, ppm) 3.55 (2H, d, J = 7.2 Hz, Ar-C**H**$_2$-CH=), 5.30 (2H, s, N-CH_2), 6.75-7.88 (14H, m, ArH and -CH=CH- (*trans*)), 10.72 (1H, s, Ar-NH-); ms (m/z) 340 (M^+, 0.3), 205 (11.9), 193 (10.6), 134 (14.0). Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.17; H, 5.95; N, 8.21.

1-[2-(1-Propenyl)benzyl]benzimidazolin-2-one (4j): Compound (**3**) (92 mg, 0.325 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of acetaldehyde (71 mg, 1.63 mmol) in dried THF (10 ml). Chromatography of the residue gave **4j** (a mixture of *cis*- and *trans*-isomers in 49:51 ratio, 60 mg, 93%): mp 135-137 °C (from CH_2Cl_2 + *n*-hexane): Ir (KBr) (υ, cm^{-1}) 3650-2600, 3140, 3060, 2942, 2920, 1701, 1673, 1618, 1490, 1435, 1395, 1312, 750, 740, 690; ^1H nmr (200 MHz, $CDCl_3$, δ, ppm) 1.67 (dd, J = 7.1, 1.7 Hz, CH_3), 1.91 (dd, J = 6.6, 1.5 Hz, CH_3), 5.07 (s, N-CH_2), 5.15 (s, N-CH_2), 5.92 (dq, J = 11.3, 7.0 Hz, HC=C**H**-CH_3 (*cis*)), 6.10 (dq, J = 15.5, 6.6 Hz, HC=C**H**-CH_3 (*trans*)), 6.55-7.44 (9H, m, ArH and Ar-CH=), 10.16 (1H, s, Ar-NH-); ms (m/z) 264 (M^+, 20.2), 134 (20.0), 131 (100). Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.29; H, 6.11; N, 10.56. Elution with a mixture of *n*-hexane and EtOAc (1:2) gave **3** (23 mg, 25%).

1-[*trans*-2-(1-Butenyl)benzyl]benzimidazolin-2-one (4k): Compound (**3**) (117 mg, 0.412 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of *n*-butyraldehyde (149 mg, 2.06 mmol) in dried THF (10 ml). Chromatography of the residue gave **4k** (112 mg, 93%): mp 119-120 °C (from CH_2Cl_2 + *n*-hexane): Ir (KBr) (υ, cm^{-1}) 3650-2600, 3100, 2950, 1701, 1690, 1670, 1620, 1483, 1399, 1141, 973 (*trans*), 750, 731, 693; ^1H nmr (60 MHz, $CDCl_3$, δ, ppm) 0.94 (3H, t, J = 7.4 Hz, CH_3), 1.46 (2H, sextet, J = 7.4 Hz CH_2), 2.16 (2H, q, J = 7.4 Hz, CH=CH-CH_2), 5.17 (2H, s, N-CH_2), 5.89-6.26 (1H, m, Ar-CH=C**H** (*trans*)), 6.69-7.39 (9H, m, ArH and Ar-C**H**= (*trans*)), 9.74 (1H, s, Ar-NH-); ms (m/z) 292 (M^+, 7.2), 143 (11.1), 134 (8.2), 192 (28.1), 129 (100). Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.89; N, 9.58. Found: C, 78.08; H, 6.84; N, 9.59.

1-[2-(Cyclohexylidenemethyl)benzyl]benzimidazolin-2-one (4l): Compound (**3**) (118 mg, 0.414 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of cyclohexanone (203 mg, 2.07 mmol) in dried THF (10 ml). Chromatography of the residue gave **4l** (107 mg, 91%): mp 141-142 °C (from CH_2Cl_2 + *n*-hexane): Ir (KBr) (υ, cm^{-1}) 3150-3100, 2935, 2850, 1703, 1485, 1398, 1148, 1012, 800, 755, 730, 685; ^1H nmr (80 MHz, $CDCl_3$, δ, ppm) 1.24-1.72 (6H, m, 3CH_2), 2.02-2.28 (4H, m, =C(CH_2-)$_2$), 5.09 (2H, s, N-CH_2), 6.31 (1H, s, =CH), 6.60-7.25 (8H, m, ArH), 10.22 (1H, s, Ar-NH-); ms (m/z) 332 (M^+, 7.2), 134 (27.0), 192 (28.1), 184 (11.1), 129 (100), Anal. Calcd for $C_{21}H_{22}N_2O$: C, 79.21; H, 6.96; N, 8.80. Found: C, 79.10; H, 7.01; N, 8.80.

1-[2-(2-Phenyl-1-butenyl)benzyl]benzimidazolin-2-one (4m): Compound (**3**) (147 mg, 0.517 mmol) was treated with *n*-BuLi (2.5 equiv.), followed by addition of propiophenone (208 mg, 1.55 mmol) in dried THF (10 ml). Chromatography of the residue gave **4m** (20 mg, 14%). The yield was obtained by integration of ^1H

nmr spectrum: ^{1}H Nmr (80 MHz, $CDCl_3$, δ, ppm) 0.90 (3H, t, J = 7.2 Hz, CH_3), 4.55 (2H, q, J = 7.2 Hz, CH_2) 5.66 (2H, s, N-CH_2), 6.77-7.95 (14H, m, ArH and -CH=), 10.23 (1H, s. Ar-NH-). Elution with a mixture of *n*-hexane and EtOAc (1:1) gave **3** (31 mg, 21%).

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