Novel method for the synthesis of α-bromocinnamaldehydes

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A novel method for the synthesis of α-bromocinnamaldehydes from aromatic aldehydes was developed. The catalytic olefination of hydrazones of aromatic aldehydes with 2-tribromomethyl-1,3-dioxolane affords ethylene acetals of the target products in yields from moderate to good.

Key words: α-bromocinnamaldehydes, acetals, catalytic olefination, catalysis, copper salts, 2-tribromomethyl-1,3-dioxolane, hydrazones.

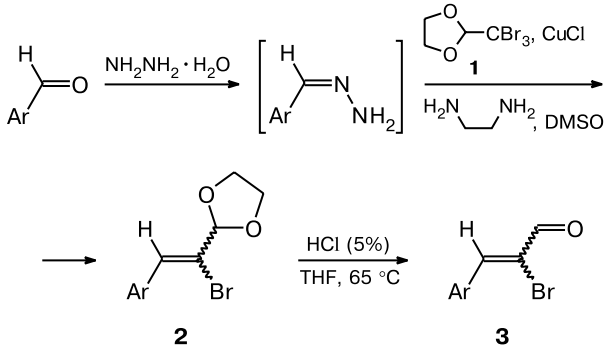
Olefination of carbonyl compounds is a versatile route for the syntheses of substituted alkenes.[1] Although many approaches are presently available, the development of new simple and efficient methods of olefination remains a typical task.[2]

We have previously[3] shown that *N*-unsubstituted hydrazones of aldehydes and ketones react with polyhaloalkanes in the presence of catalytic amounts of copper salts to transform into the corresponding substituted alkenes. Based on the catalytic olefination, we developed methods for syntheses of dihaloalkenes, vinyl halides, fluorine-containing alkenes, and chlorocinnamic nitriles and esters. A possible reaction mechanism has been discussed earlier.[4]

In the present work, we propose a novel method for the synthesis of α-bromocinnamaldehydes using catalytic olefination, which is a convenient alternative to the known methods for the preparation of these compounds, such as the Wittig reaction,[5] elimination of HBr from 2,3-dibromo-3-arylpropionaldehydes,[6,7] and bromination of cinnamaldehydes.[8] α-Bromocinnamaldehydes are valuable bifunctional building blocks and can be used in syntheses of heterocyclic systems.[9]

We showed that treatment of 4-chlorobenzaldehyde with bromal produced no 2-bromo-3-(4-chlorophenyl)acrylaldehyde, and symmetrical 4-chlorobenzaldehyde azine was the only reaction product according to the GLC-MS data. To prevent the transformation of hydrazone into azine, we used bromal acetal, *viz.*, 2-tribromomethyl-1,3-dioxolane (**1**), as the polyhalogen-containing reagent (Scheme 1). The influence of conditions (the nature of solvent and base, the amount of catalyst and reactant **1**) on the course of the reaction was studied. The highest yield of unsaturated aldehyde acetal was observed for the reaction in DMSO with threefold excess of acetal **1**, ethylenediamine as a base, and copper(I) chloride (10 mol.%). It should be mentioned that the reaction is rather fast (it takes about 3 h according to TLC). The reaction can also be performed as a one-pot process. In the case of the reaction with 4-chlorobenzaldehyde, the yield of the target product was virtually independent of whether the hydrazone was obtained *in situ* or isolated preliminarily.

Scheme 1



We applied the developed method to synthesize ethylene acetals of different α-bromocinnamaldehydes **2** from aromatic and heteroaromatic aldehydes (Table 1). Subsequent treatment of ethylene acetals **2** with 5% HCl in THF afforded the corresponding α-bromocinnamaldehydes **3a—i** in high yields (see Table 1). According to the GLC-MS data, the ratio of *Z*- to *E*-isomers remains un-

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Table 1. Yields of α-bromocinnamaldehydes **3** and their ethylene acetals **2**

Compounds	Ar	Yield (%)		Ratio of *Z*- : *E*-isomers
		2	**3**	
2a, 3a	Ph	62	93	9 : 1
2b, 3b	4-$MeOC_6H_4$	69	95	12 : 1
2c, 3c	4-ClC_6H_4	66	89	10 : 1
2d, 3d	4-$NO_2C_6H_4$	48	92	10 : 1
2e, 3e	3-$NO_2C_6H_4$	51	94	9 : 1
2f, 3f	2-$NO_2C_6H_4$	52	94	9 : 1
2g, 3g	3,4-$(MeO)_2C_6H_3$	68	95	14 : 1
2h, 3h	2-Naphthyl	66	93	9 : 1
2i, 3i	3-Pyridyl	54	90	9 : 1

changed on going from acetals to aldehydes. As shown by a comparison of the chemical shifts in the ^{13}C NMR spectra of the main isomer of compound **3a** with the earlier published data,[10] the main reaction product is the *Z*-isomer. Based on the characteristic signals of the C atoms of the double bond (δ 146.7—151.8 and 123.5—125.7) and aldehyde group (δ 186.3—187.0), we assigned all the other compounds to *Z*-isomers. It should be mentioned that the stereoselectivity of catalytic olefination with 2-tribromomethyldioxolane is higher, on the average, than that with trichloroacetonitrile and ethyl trichloroacetate.[3]

Thus, a novel efficient method for the synthesis of different α-bromocinnamaldehydes and their acetals from accessible reagents under mild conditions was developed. The high stereoselectivity of formation of the target products is one of the most important advantages of the reaction proposed.

Experimental

IR spectra were obtained on a UR-20 spectrophotometer in Nujol. ^1H and ^{13}C NMR spectra were obtained on a Varian VXR-400 spectrometer (400 and 100 MHz) in $CDCl_3$ using Me_4Si as the internal standard. Mass spectra were recorded on a Finnigan SSQ 7000 mass spectrometer (EI, 70 eV) connected with a Varian 3400 GC gas chromatograph equipped with a DB-5MS column (30 m × 0.2 mm, helium as carrier gas). The *m/z* values are presented for ^{79}Br and ^{35}Cl isotopes. Merck 60 F_{254} plates were used for TLC (hexane—CH_2Cl_2, 1 : 2), and column chromatography was carried out on silica gel Merck (63—200 mesh). Melting points were measured for mixtures of isomers without recrystallization.

2-Tribromomethyl-1,3-dioxolane (**1**) was synthesized according to a previously published procedure.[11]

Commercial reagents and solvents were used. DMSO was reagent grade. The purity of the aldehydes used was not below than 95%.

Synthesis of ethylene acetals of α-bromocinnamaldehydes (2). A solution of an aldehyde (3 mmol) in DMSO (1 mL) was added dropwise with stirring to a solution of hydrazinehydrate (0.15 mL, 3 mmol) in DMSO (1 mL). The mixture was stirred until the starting aldehyde disappeared (TLC). Ethylenediamine (1.0 mL, 15 mmol) and freshly purified[12] CuCl (30 mg, 0.3 mmol) were added to the solution of the resulting hydrazone, and then a solution of **1** (2.9 g, 9 mmol) in DMSO (2 mL) was added dropwise for 2 min at 18—20 °C (cooling). The reaction mixture was stirred for 3 h and treated with 0.1 *M* HCl (150 mL). The reaction products were extracted with CH_2Cl_2 (3×50 mL), and the combined extracts were dried with Na_2SO_4. The solvent was distilled off *in vacuo*, and the reaction products were isolated by column chromatography.

2-(1-Bromo-2-phenylvinyl)-1,3-dioxolane (2a), mixture of isomers (*Z* : *E* = 9 : 1), white crystals, m.p. 77 °C, R_f 0.42. IR, ν/cm^{-1}: 1641 (C=C). ^1H NMR of *Z*-isomer, δ: 7.68—7.64 (m, 2 H); 7.39—7.30 (m, 3 H); 7.22 (s, 1 H, HC=); 5.47 (s, 1 H); 4.22—4.14, 4.07—3.99 (both m, 2 H each). ^{13}C NMR of *Z*-isomer, δ: 134.3, 131.3, 129.3, 128.6, 128.2, 123.2, 105.1, 65.8 (CH_2). Mass spectrum, *m/z* (I_{rel} (%)): 254 $[M]^+$ (17), 175 $[M - Br]^+$ (100), 131 $[M - Br - C_2H_4O]$ (35), 77 $[C_6H_5]^+$ (13), 73 $[C_3H_5O_2]^+$ (74). Found (%): C, 51.85; H, 4.33. $C_{11}H_{11}BrO_2$. Calculated (%): C, 51.79; H, 4.35.

2-[1-Bromo-2-(4-methoxyphenyl)vinyl]-1,3-dioxolane (2b), mixture of isomers (*Z* : *E* = 12 : 1), white crystals, m.p. 82 °C, R_f 0.22. IR, ν/cm^{-1}: 1622 (C=C). ^1H NMR of *Z*-isomer, δ: 7.67 (d, 2 H, *J* = 9.0 Hz); 7.14 (s, 1 H, HC=); 6.89 (d, 2 H, *J* = 9.0 Hz); 5.44 (s, 1 H); 4.21—4.13, 4.06—3.98 (both m, 2 H each); 3.82 (s, 1 H, Me). ^{13}C NMR of *Z*-isomer, δ: 159.8, 130.9, 126.7, 120.9, 113.6, 105.4, 65.8 (CH_2), 55.2 (Me). Mass spectrum, *m/z* (I_{rel} (%)): 284 $[M]^+$ (33), 253 $[M - Me]^+$ (14), 205 $[M - Br]^+$ (100), 161 $[M - Br - C_2H_4O]^+$ (47), 73 $[C_3H_5O_2]^+$ (68). Found (%): C, 50.85; H, 4.78. $C_{12}H_{13}BrO_3$. Calculated (%): C, 50.55; H, 4.60.

2-[1-Bromo-2-(4-chlorophenyl)vinyl]-1,3-dioxolane (2c), mixture of isomers (*Z* : *E* = 10 : 1), white crystals, m.p. 62—64 °C, R_f 0.44. IR, ν/cm^{-1}: 1640 (C=C). ^1H NMR of *Z*-isomer, δ: 7.60, 7.33 (both d, 2 H each, *J* = 8.6 Hz); 7.17 (s, 1 H, HC=); 5.45 (s, 1 H); 4.21—4.14, 4.07—4.00 (both m, 2 H each). ^{13}C NMR of *Z*-isomer, δ: 134.5, 132.8, 130.6, 130.0, 128.5, 124.1, 105.0, 65.8 (CH_2). Mass spectrum, *m/z* (I_{rel} (%)): 288 $[M]^+$ (14), 253 $[M - Cl]^+$ (15), 209 $[M - Br]^+$ (77), 73 $[C_3H_5O_2]^+$ (100). Found (%): C, 45.58; H, 3.49. $C_{11}H_{10}BrClO_2$. Calculated (%): C, 45.63; H, 3.48.

2-[1-Bromo-2-(4-nitrophenyl)vinyl]-1,3-dioxolane (2d), mixture of isomers (*Z* : *E* = 10 : 1), yellow crystals, m.p. 138—140 °C, R_f 0.26. IR, ν/cm^{-1}: 1520 (NO_2), 1350 (NO_2). ^1H NMR of *Z*-isomer, δ: 8.22, 7.79 (both d, 2 H each, *J* = 8.8 Hz); 7.29 (s, 1 H, HC=); 5.49 (s, 1 H); 4.20—4.14, 4.09—4.03 (both m, 2 H each). ^{13}C NMR of *Z*-isomer, δ: 147.3, 140.9, 130.0, 129.0, 127.6, 123.5, 104.6, 65.9 (CH_2). Mass spectrum, *m/z* (I_{rel} (%)): 299 $[M]^+$ (4), 207 $[M - Br - C_2H_4O]^+$ (20), 220 $[M - Br]^+$ (100), 73 $[C_3H_5O_2]^+$ (89). Found (%): C, 43.94; H, 3.16. $C_{11}H_{10}BrNO_4$. Calculated (%): C, 44.02; H, 3.36.

2-[1-Bromo-2-(3-nitrophenyl)vinyl]-1,3-dioxolane (2e), mixture of isomers (*Z* : *E* = 9 : 1), brown crystals, m.p. 42 °C, R_f 0.31. IR, ν/cm^{-1}: 1538 (NO_2), 1355 (NO_2). ^1H NMR of *Z*-isomer, δ: 8.52 (s, 1 H); 8.17, 7.95 (both d, 1 H each, *J* = 7.9 Hz); 7.54 (t, 1 H, *J* = 7.9 Hz); 7.28 (s, 1 H, HC=); 5.49 (s, 1 H); 4.20—4.14, 4.09—4.03 (both m, 2 H each). ^{13}C NMR of *Z*-isomer, δ: 147.3, 133.3, 131.8, 131.1, 129.1, 128.4, 126.7, 124.7, 103.8, 65.5 (CH_2). Mass spectrum, *m/z* (I_{rel} (%)): 299 $[M]^+$ (3), 220 $[M - Br]^+$ (87), 73 $[C_3H_5O_2]^+$ (100).

Found (%): C, 43.90; H, 3.19. $C_{11}H_{10}BrNO_4$. Calculated (%): C, 44.02; H, 3.36.

2-[1-Bromo-2-(2-nitrophenyl)vinyl]-1,3-dioxolane (2f), mixture of isomers (*Z* : *E* = 9 : 1), yellow crystals, m.p. 68 °C, R_f 0.24. IR, ν/cm^{-1}: 1535 (NO_2), 1350 (NO_2). ^{1}H NMR of *Z*-isomer, δ: 8.11 (d, 1 H, *J* = 8.2 Hz); 7.65—7.61 (m, 2 H); 7.57 (s, 1 H, HC=); 7.50 (t, 1 H, *J* = 8.2 Hz); 5.59 (s, 1 H); 4.19—4.14, 4.08—4.03 (both m, 2 H each). ^{13}C NMR of *Z*-isomer, δ: 148.1, 136.1, 135.0, 129.2, 128.6, 126.8, 124.0, 123.2, 104.6, 65.8 (CH_2). Mass spectrum, *m*/*z* (I_{rel} (%)): 299 $[M]^+$ (1), 220 $[M - Br]^+$ (3), 73 $[C_3H_5O_2]^+$ (100). Found (%): C, 43.84; H, 3.30. $C_{11}H_{10}BrNO_4$. Calculated (%): C, 44.02; H, 3.36.

2-[1-Bromo-2-(3,4-dimethoxyphenyl)vinyl]-1,3-dioxolane (2g), mixture of isomers (*Z* : *E* = 14 : 1), white crystals, m.p. 60 °C, R_f 0.11. IR, ν/cm^{-1}: 1633 (C=C). ^{1}H NMR of *Z*-isomer, δ: 7.40 (s, 1 H); 7.21 (d, 1 H, *J* = 8.4 Hz); 7.14 (s, 1 H, HC=); 6.85 (d, 1 H, *J* = 8.4 Hz); 5.44 (s, 1 H); 4.19—4.14, 4.06—3.99 (both m, 2 H each); 3.88 (s, 6 H, Me). ^{13}C NMR of *Z*-isomer, δ: 149.4, 148.3, 130.9, 126.9, 123.0, 121.0, 112.1, 110.6, 105.4, 65.8 (CH_2), 55.84 (Me), 55.82 (Me). Mass spectrum, *m*/*z* (I_{rel} (%)): 314 $[M]^+$ (26), 283 $[M - MeO]^+$ (25), 235 $[M - Br]^+$ (45), 73 $[C_3H_5O_2]^+$ (100). Found (%): C, 49.83; H, 4.88. $C_{13}H_{15}BrO_4$. Calculated (%): C, 49.54; H, 4.80.

2-[1-Bromo-2-(2-naphthyl)vinyl]-1,3-dioxolane (2h), mixture of isomers (*Z* : *E* = 9 : 1), white crystals, m.p. 102—104 °C, R_f 0.55. IR, ν/cm^{-1}: 1635 (C=C). ^{1}H NMR of *Z*-isomer, δ: 8.15 (s, 1 H); 7.86—7.77 (m, 4 H); 7.51—7.45 (m, 2 H); 7.39 (s, 1 H, HC=); 5.53 (s, 1 H); 4.25—4.16, 4.10—4.00 (both m, 2 H each). ^{13}C NMR of *Z*-isomer, δ: 133.2, 132.9, 131.8, 131.3, 129.1, 128.3, 127.69, 127.63, 126.64, 126.57, 126.3, 123.62, 105.2, 65.8 (CH_2). Mass spectrum, *m*/*z* (I_{rel} (%)): 304 $[M]^+$ (70), 225 $[M - Br]^+$ (83), 151 $[M - Br - C_3H_5O_2]^+$ (33), 73 $[C_3H_5O_2]^+$ (74). Found (%): C, 59.15; H, 4.60. $C_{15}H_{13}BrO_2$. Calculated (%): C, 59.04; H, 4.29.

2-[1-Bromo-2-(3-pyridyl)vinyl]-1,3-dioxolane (2i), mixture of isomers (*Z* : *E* = 9 : 1), yellow crystals, m.p. 38 °C, R_f 0.45 (ethyl acetate). IR, ν/cm^{-1}: 1642 (C=C). ^{1}H NMR of *Z*-isomer, δ: 8.74 (s, 1 H); 8.54 (d, 1 H, *J* = 4.7 Hz); 8.11 (d, 1 H, *J* = 8.0 Hz); 7.29 (dd, 1 H, *J* = 8.0 Hz, *J* = 4.7 Hz); 7.20 (s, 1 H, HC=); 5.47 (s, 1 H); 4.18—4.12, 4.07—4.01 (both m, 2 H each). ^{13}C NMR of *Z*-isomer, δ: 150.6, 149.4, 135.8, 130.4, 127.7, 126.1, 123.0, 104.7, 65.8 (CH_2). Mass spectrum, *m*/*z* (I_{rel} (%)): 255 $[M]^+$ (7), 176 $[M - Br]^+$ (100), 73 $[C_3H_5O_2]^+$ (61). Found (%): C, 46.06; H, 4.00. $C_{10}H_{10}BrNO_2$. Calculated (%): C, 46.90; H, 3.94.

Synthesis of α-bromocinnamaldehydes 3. To a solution of ethylene acetal **2** (1 mmol) in THF (2 mL), 5% HCl (1 mL) was added. The reaction mixture was stirred for 5 h at 65 °C, after which water (30 mL) was added. The reaction products were extracted with CH_2Cl_2 (3×20 mL), and the combined extracts were dried with Na_2SO_4. The solvent was distilled off *in vacuo*. Aldehydes **3** were obtained as mixtures of *Z*,*E*-isomers.

2-Bromo-3-phenylprop-2-enal (3a) (*Z* : *E* = 9 : 1), white crystals, m.p. 70—71 °C. ^{1}H NMR of *Z*-isomer, δ: 9.34 (s, 1 H, CHO); 8.03—7.98 (m, 2 H); 7.89 (s, 1 H, HC=); 7.50—7.47 (m, 3 H). ^{13}C NMR of *Z*-isomer, δ: 187.0 (CHO), 149.1, 132.9, 131.6, 130.9, 128.7, 124.2. The NMR spectra correspond to published data.[10]

2-Bromo-3-(4-methoxyphenyl)prop-2-enal (3b) (*Z* : *E* = 12 : 1), white crystals, m.p. 61 °C, R_f 0.22. IR, ν/cm^{-1}: 1715 (C=O), 1635 (C=C). ^{1}H NMR of *Z*-isomer, δ: 9.29 (s, 1 H, CHO); 8.02 (d, 2 H, *J* = 8.8 Hz); 7.80 (s, 1 H, HC=); 6.99 (d, 2 H, *J* = 8.8 Hz); 3.87 (s, 3 H, Me). ^{13}C NMR of *Z*-isomer, δ: 186.9 (CHO), 162.4, 148.8, 133.3, 125.6, 121.7, 114.2, 55.5 (Me). Mass spectrum, *m*/*z* (I_{rel} (%)): 240 $[M]^+$ (69), 161 $[M - Br]^+$ (100), 108 $[C_7H_8O]^+$ (63). Found (%): C, 49.65; H, 3.80. $C_{10}H_9BrO_2$. Calculated (%): C, 49.82; H, 3.76.

2-Bromo-3-(4-chlorophenyl)prop-2-enal (3c) (*Z* : *E* = 10 : 1), white crystals, m.p. 91 °C, R_f 0.44. IR, ν/cm^{-1}: 1690 (C=O). ^{1}H NMR of *Z*-isomer, δ: 9.33 (s, 1 H, CHO); 7.94 (d, 2 H, *J* = 8.6 Hz); 7.84 (s, 1 H, HC=); 7.45 (d, 2 H, *J* = 8.6 Hz). ^{13}C NMR of *Z*-isomer, δ: 186.8 (CHO), 147.3, 132.1, 131.3, 129.1, 124.8. Mass spectrum, *m*/*z* (I_{rel} (%)): 244 $[M]^+$ (29), 209 $[M - Cl]^+$ (49), 165 $[M - Br]^+$ (15), 75 $[C_6H_3]^+$ (100). Found (%): C, 44.15; H, 2.47. C_9H_6ClBrO. Calculated (%): C, 44.03; H, 2.46.

2-Bromo-3-(4-nitrophenyl)prop-2-enal (3d) (*Z* : *E* = 10 : 1), white crystals, m.p. 136 °C, R_f 0.31. IR, ν/cm^{-1}: 1695 (C=O), 1522 (NO_2), 1350 (NO_2). ^{1}H NMR of *Z*-isomer, δ: 9.40 (s, 1 H, CHO); 8.32, 8.10 (both d, 2 H each, *J* = 8.8 Hz); 7.96 (s, 1 H, HC=). ^{13}C NMR of *Z*-isomer, δ: 186.4 (CHO), 148.7, 145.2, 138.9, 131.2, 127.9, 123.8. Mass spectrum, *m*/*z* (I_{rel} (%)): 255 $[M]^+$ (12), 209 $[M - NO_2]^+$ (11), 176 $[M - Br]^+$ (12), 28 $[CO]^+$ (100). Found (%): C, 42.15; H, 2.50. $C_9H_6BrNO_3$. Calculated (%): C, 42.22; H, 2.36.

2-Bromo-3-(3-nitrophenyl)prop-2-enal (3e) (*Z* : *E* = 9 : 1), white crystals, m.p. 89—91 °C, R_f 0.33. IR, ν/cm^{-1}: 1695 (C=O), 1528 (NO_2), 1352 (NO_2). ^{1}H NMR of *Z*-isomer, δ: 9.40 (s, 1 H, CHO); 8.85 (s, 1 H); 8.34, 8.27 (both d, 1 H each, *J* = 8.0 Hz); 7.97 (s, 1 H, HC=); 7.68 (y, 1 H, *J* = 8.0 Hz). ^{13}C NMR of *Z*-isomer, δ: 186.3 (CHO), 148.4, 145.1, 135.9, 134.5, 129.9, 127.1, 125.5, 125.1. Mass spectrum, *m*/*z* (I_{rel} (%)): 255 $[M]^+$ (25), 238 $[M - O - H]^+$ (79), 208 $[M - NO_2]^+$ (30), 176 $[M - Br]^+$ (20), 102 $[C_8H_6]^+$ (100). Found (%): C, 42.14; H, 2.21. $C_9H_6BrNO_3$. Calculated (%): C, 42.22; H, 2.36.

2-Bromo-3-(2-nitrophenyl)prop-2-enal (3f) (*Z* : *E* = 9 : 1), white crystals, m.p. 94 °C, R_f 0.35. IR, ν/cm^{-1}: 1700 (C=O), 1525 (NO_2), 1352 (NO_2). ^{1}H NMR of *Z*-isomer, δ: 9.46 (s, 1 H, CHO); 8.33 (s, 1 H); 8.23 (d, 1 H, *J* = 8.4 Hz); 7.77—7.75 (m, 2 H); 7.67—7.61 (m, 1 H). ^{13}C NMR of *Z*-isomer, δ: 186.0 (CHO), 146.7, 146.4, 133.8, 131.0, 130.8, 129.5, 128.1, 125.1. Mass spectrum, *m*/*z* (I_{rel} (%)): 255 $[M]^+$ (1), 176 $[M - Br]^+$ (20), 92 $[CHBr]^+$ (100). Found (%): C, 42.50; H, 2.38. $C_9H_6BrNO_3$. Calculated (%): C, 42.22; H, 2.36.

2-Bromo-3-(3,4-dimethoxyphenyl)prop-2-enal (3g) (*Z* : *E* = 14 : 1), white crystals, m.p. 62 °C, R_f 0.11. IR, ν/cm^{-1}: 1685 (C=O). ^{1}H NMR of *Z*-isomer, δ: 9.29 (s, 1 H, CHO); 7.80 (br.s, 2 H, Ar and HC=); 7.52, 6.95 (both d, 1 H each, *J* = 8.4 Hz); 3.94, 3.93 (both s, 3 H each, Me). ^{13}C NMR of *Z*-isomer, δ: 186.9 (CHO), 152.1, 149.1, 148.7, 126.6, 125.7, 121.6, 112.8, 110.8, 56.0 (Me), 55.9 (Me). Mass spectrum, *m*/*z* (I_{rel} (%)): 270 $[M]^+$ (68), 191 $[M - Br]^+$ (51), 120 $[M - Br - C_2H_2O - MeO]^+$ (89), 92 $[C_6H_2O]^+$ (100). Found (%): C, 48.25; H, 4.42. $C_{11}H_{11}BrO_3$. Calculated (%): C, 48.73; H, 4.09.

2-Bromo-3-(2-naphthyl)prop-2-enal (3h) (*Z* : *E* = 9 : 1), white crystals, m.p. 125—126 °C, R_f 0.38. IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR of *Z*-isomer, δ: 9.39 (s, 1 H, CHO); 8.49 (s, 1 H); 8.10—8.04 (m, 2 H); 7.94—7.85 (m, 3 H); 7.61—7.53 (m, 2 H). ^{13}C NMR of *Z*-isomer, δ: 187.0 (CHO), 149.1, 134.5, 132.8, 132.3, 130.4, 129.1, 128.4, 128.3, 127.8, 126.9, 126.7, 124.2. Mass spectrum, *m*/*z* (I_{rel} (%)): 260 $[M]^+$ (41), 181 $[M - Br]^+$ (26), 151 $[M - Br - CHO]^+$ (100), 28 $[CO]^+$ (100).

Found (%): C, 59.35; H, 3.80. $C_{13}H_9BrO$. Calculated (%): C, 59.80; H, 3.47.

2-Bromo-3-(3-pyridyl)prop-2-enal (3i) (*Z* : *E* = 10 : 1), brown crystals, m.p. 55 °C, R_f 0.38 (ethyl acetate). IR, ν/cm^{-1}: 1689 (C=O), 1609 (C=C). ^{1}H NMR of *Z*-isomer, δ: 9.37 (s, 1 H, CHO); 8.99 (s, 1 H); 8.69 (d, 1 H, *J* = 4.7 Hz); 8.50 (d, 1 H, *J* = 7.8 Hz); 7.90 (s, 1 H, HC=); 7.43 (dd, 1 H, *J* = 7.8 Hz, *J* = 4.7 Hz). ^{13}C NMR of *Z*-isomer, δ: 186.4 (CHO), 152.0, 151.8, 144.9, 136.7, 129.2, 126.5, 123.5. Mass spectrum, *m*/*z* (I_{rel} (%)): 211 $[M]^+$ (66), 132 $[M - Br]^+$ (100), 7 $[C_5H_3N]^+$ (51). Found (%): C, 45.15; H, 2.80. C_8H_6BrNO. Calculated (%): C, 45.31; H, 2.85.

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