

# Photolysis of Baylis-Hillman Acetates: Homolytic vs. Heterolytic Cleavage

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## ABSTRACT

Photochemical behaviour of Baylis-Hillman (BH) acetates were studied in presence of 254 nm irradiation. It was found that they underwent C-O bond cleavage to give rise to products. Analysis of the products showed that the bond cleavage is homolytic in nature. This homolytic cleavage results in formation of radical pair which may undergo decarboxylation followed by radical-radical coupling or photo rearrangement to give products.

**Keywords :** Electron transfer, Photolysis, Radicals, Singlet Oxygen, Sensitizer, Baylis-Hillman acetates

## 1 INTRODUCTION

Photochemistry of arylmethyl compounds with leaving groups has been subject of research for last few decades [1-3]. The reaction is important from mechanistic as well as synthetic point of view. Photochemical cleavage of benzylic-leaving group can follow either heterolytic (ion pair formation) or homolytic (radical pair formation) pathway. One of the earliest examples was reported by Zimmerman on photolysis of methoxy substituted benzyl acetates and proposed generation of ion pair intermediate through heterolytic cleavage for product formation [4-7]. Later on more detailed studies on several substituted arylcarboxylates, radical pair formation through homolytic cleavage has been established as major pathway for product formation [1,8-12]. When carboxylates are leaving groups cleavage takes place from the  $S_1$  state (as the triplet state is unreactive) where  $k_R \gg k_I$ ,  $k_R$  and  $k_I$  are the rate constants for formation radical pair and that of ion pair respectively (Scheme 1) [9].

BH acetates are special class of benzyl acetates having a vinylic substituent present at  $\alpha'$  position [13-15]. These are very useful synthetic intermediates and find applications in numerous chemical transformations. In continuation of our research on Baylis-Hillman chemistry and photochemistry [16-20], herein we are going to disclose the result of our study of photochemical reaction of BH acetates under UV irradiation. It was observed that the acetates underwent C-O bond cleavage through homolytic pathway to give products.

## 2 RESULTS AND DISCUSSION

Baylis Hillman acetates 1-5 were prepared according to literature procedure [13]. Compound 1 was selected for initial study. 0.01 M solution of 1 in hexane was taken in a quartz tube and after degassing irradiated in a Rayonet Reactor fitted with eight tubes of 254 nm under inert condition. Progress of reaction was monitored by GC-MS. Maximum conversion (67%) of 1 was observed after 21h of irradiation. Formation of

four products were observed by GC-MS. Purification of crude reaction mixture led to isolation of all the four products which on characterisation by spectral techniques found to be 1a, 1b, 1c and 1d. All other BH acetates were irradiated accordingly and products 2a-5a, 2b-5b, 2c-5c and 2d-5d were isolated (Scheme 2).

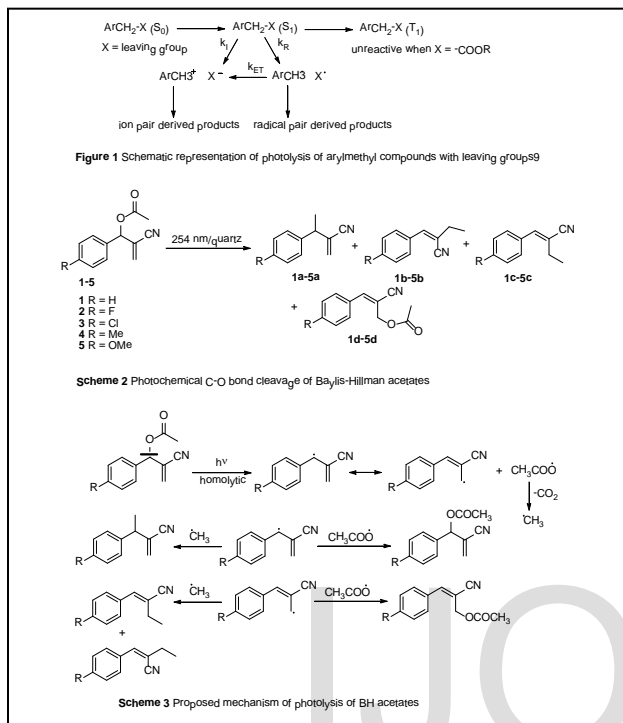
When irradiation was carried out in alcoholic solvent like methanol or isopropanol resulted in a complex mixture (formation of many non identifiable products) as it was monitored by GC-MS. Using various concentrations of 1 also yielded no result. When acetonitrile (0.01M solution) was used as solvent for irradiation the reactions proceeded well to form products though with less degree of % conversions of starting material (Table 1).

The photochemical reactions were also carried out using 450W medium pressure Hg arc lamp in an immersion well using hexane as solvent under inert condition. Under this condition all the acetates were irradiated for 2 h when maximum conversion of starting material was observed by GC MS. So time of irradiation can be reduced to 2h by this method.

Time dependent study was also carried out for compound 1 using 450W medium pressure Hg lamp in immersion well (Table 3).

Analysis of products showed that they are results of homolytic C-O bond cleavage as products 1a-5a, 1b-5b, 1c-5c and 1d-5d are radical-radical coupling product. So homolytic cleavage of C-O bond had taken place. This homolytic cleavage results in formation of stable benzyl radical I and acetate radical. This benzyl radical I can exist as another stable canonical form allyl radical. Acetate radical generated methyl radical by decarboxylation. Coupling of the methyl radical with benzyl radical yielded products 1a-5a (Scheme 3). Coupling of methyl radical with allyl radical produced diastereomeric products 1b-5b (Z isomer) and 1c-5c (E isomer). The stereochemical configurations of these isomeric products were assigned based on chemical shift ( $\delta$ ) of the  $\beta$ -vinylic proton in  $^1H$

NMR spectra [21-22]. The acetate radical itself coupled with the allyl radical (II) before decarboxylation to provide compounds **1d-5d**. The stereochemistry for these set of compounds were also determined on the basis of  $\delta$  value of  $\beta$ -vinylic protons.



### 3 CONCLUSION

Photolysis of various Baylis-Hillman acetates was carried out under UV irradiation. Analysis of the products led to conclusion that photolysis took place through intermediate formation of radical pair. This study supports the photochemical homolytic cleavage of benzyl acetates.

### 4 EXPERIMENTAL

#### General Methods

All the chemicals and reagents were purchased from commercial sources. Chromatographic purifications were carried out on silica 100-200 mesh. IR spectra (KBr matrix) were recorded using a Thermo Nicolet Nexus 670 FTIR spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on either a Bruker Avance 300-MHz FT spectrometer. Chemical shifts ( $\delta$ ) are quoted in parts per million and are referenced to tetramethylsilane (TMS) as internal standard. Coupling constants (*J*) are given in Hz.

#### Typical experimental procedures for irradiation of BH acetates in a Rayonet reactor using 254nm tube

0.01 M solution of BH acetate in hexane or acetonitrile was taken in a quartz tube and after degassing placed in a Rayonet reactor fitted with eight tubes of 254nm. The irradiation was

**Table 1** Photochemical irradiation of BH acetates using 254 nm irradiation<sup>a</sup>

Sl no.	Compound	Solvent	% conversion <sup>b</sup>	yield photoproducts (%)			
				1a-5a	1b-5b	1c-5c	1d-5d
1	1	Hexane	67	15	18	03	18
		Acetonitrile	54	11	15	05	11
2	2	Hexane	66	12	16	10	17
		Acetonitrile	49	10	13	08	07
3	3	Hexane	65	11	23	0	17
		Acetonitrile	38	08	15	0	04
4	4	Hexane	69	12	16	10	17
		Acetonitrile	50	10	13	08	07
5	5	Hexane	60	10	22	11	05
		Acetonitrile	39	04	11	06	07

<sup>a</sup> 0.01M solution of BH acetates taken in a quartz tube was irradiated with 254 nm tube under inert condition for 21h; <sup>b</sup> % conversion was determined by GC-MS; <sup>c</sup> yields are isolated yield.

**Table 2** Photochemical irradiation of BH acetates using 450W medium pressure Hg lamp

Sl no.	Compound	Solvent	% conversion <sup>a</sup>	yield of photoproducts (%) <sup>b</sup>			
				1a-5a	1b-5b	1c-5c	1d-5d
1	1a	Hexane	73	11	25	04	17
2	1b	Hexane	76	13	17	12	20
3	1c	Hexane	77	12	33	0	19
4	1d	Hexane	71	14	34	09	04
5	1e	Hexane	61	07	26	10	07

<sup>a</sup>determined by GC-MS analysis; <sup>b</sup>isolated yield.

**Table 3** Time dependent distribution of photoproducts (%) for irradiation of 1a

Sl no.	Time of Irradiation (min)	% conversion <sup>b</sup>	photoproducts (%) <sup>b</sup>			
			1a	1b	1c	
1	15	16	03	07	02	04
2	30	33	06	15	04	08
3	45	42	07	21	05	09
4	60	53	07	26	06	14
5	75	59	08	27	06	18
6	105	70	13	30	07	20
7	120	73	14	31	07	21

<sup>a</sup> 0.01M solution of 1 was irradiated using 450W medium pressure Hg lamp in immersion well under nitrogen conditions; <sup>b</sup> % determined by GC-MS.

then carried out under nitrogen atmosphere for 21 h when maximum conversion of starting material was observed by GC MS. The irradiation tubes were then switched off; the reaction mixture was concentrated under reduced pressure to get the crude products which were purified by iterative column chromatography using silica gel 100-200 mesh (eluent hexane followed by hexane/ethyl acetate 99:1, then hexane/ethyl acetate 95:5).

#### Typical experimental procedures for irradiation of BH acetates using 450W medium pressure Hg arc lamp

0.01 M solution of BH acetate in hexane was taken in an immersion well and after degassing was irradiated using 450W medium pressure Hg arc lamp under nitrogen atmosphere for 2h (monitored by GC MS). The lamp was then switched off; the reaction mixture was concentrated under reduced pressure to get the crude products which were purified by iterative column chromatography using silica gel 100-200 mesh (eluent hexane followed by hexane/ethyl acetate 99:1, then hexane/ethyl acetate 95:5).

**2-Methylene-3-phenyl butanenitrile (1a):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  7.14-7.05 (m, 5H), 5.84 (s, 1H), 5.64 (d, 1H), 3.60 (q,  $J = 7.0$  Hz, 1H), 1.51 (d,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  143.48, 139.45, 129.43, 129.33, 129.09, 128.84, 127.12, 120.36, 43.51, 22.89; ESIMS ( $m/z$ )180  $[\text{M}+\text{Na}]^+$ ; elemental analysis cal. for  $\text{C}_{11}\text{H}_{11}\text{N}$ , C 84.04, H 7.05, N 8.91.

**3-(4-fluorophenyl)-2-methylene butanenitrile (2a):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$ NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  7.19-7.12 (m, 2H),7.10-7.05 (m, 2H), 5.92 (s, 1H), 5.73 (s, 1H), 3.70 (d,  $J = 6.8$  Hz, 1H), 1.58 (d,  $J = 7.8$  Hz, 3H );  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  164.53, 161.23, 142.30, 131.08, 130.97, 129.14, 128.89, 128.78, 120.01, 117.05, 115.99, 43.23, 22.86; ES-IMS ( $m/z$ ) 198  $[\text{M}+\text{Na}]^+$ ; elemental analysis cal. for  $\text{C}_{11}\text{H}_{10}\text{NF}$ , C 75.4; H 5.75; N 7.99.

**3-(4-chlorophenyl)-2-methylene butanenitrile (3a):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J = 6.8$  Hz, 2H),7.16 (d,  $J = 7.1$  Hz, 2H), 5.88 (s, 1H), 5.69 (s, 1H), 3.67-3.60 (m, 1H), 1.51 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  164.53, 161.23, 142.30, 131.08, 130.97, 129.14, 128.89, 128.78, 120.01, 117.05, 115.99, 43.23, 22.86; ES-IMS ( $m/z$ ) 214  $[\text{M}+\text{Na}]^+$ ; elemental analysis cal. for  $\text{C}_{11}\text{H}_{10}\text{NCl}$ , C 68.93; H 5.26; N 7.31; F 18.50.

**2-methylene-3p-tolyl butanenitrile (4a):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  7.14-7.07 (m, 4H), 5.84 (s, 1H), 5.64 (s, 1H), 3.61 (q,  $J = 7.8$  Hz, 1H), 2.34 (s, 3H), 1.51 (d,  $J = 6.8$  Hz, 3H ) ;  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ) :  $\delta$  146.18, 132.68, 128.32, 127.32, 124.04, 123.22, 116.54, 40.87, 31.39, 30.14, 29.64; ESIMS ( $m/z$ )194  $[\text{M}+\text{Na}]^+$ ; elemental analysis cal. for  $\text{C}_{12}\text{H}_{13}\text{N}$ , C 84.19; H 7.65; N 8.18.

**3-(4-methoxyphenyl)-2-methylenebutanenitrile (5a):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  6.91-6.78 (m, 4H), 5.83 (s, 1H), 5.63 (s, 1H), 3.78 (s, 3H), 3.59 (q,  $J = 7.2$  Hz, 1H), 1.52 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  146.18, 132.68, 128.32, 127.32, 124.04, 123.22, 116.54, 40.87, 31.39, 30.14, 29.64; ESIMS ( $m/z$ ) 188  $[\text{M}+\text{H}]^+$ ; elemental analysis cal. for  $\text{C}_{12}\text{H}_{13}\text{NO}$ , C 76.98, H 7.00, N 7.48.

**Z-2-benzylidene butanenitrile (1b):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69-7.70 (d, 2H ), 7.34-7.40 (m, 3H), 6.89 (s, vinylic-H, for *E* isomer it appear at 7.14), 2.47-2.42 (m, 2H), 1.28-1.26 (t,  $J = 7.8$  Hz, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  142.25, 133.93, 129.68, 128.64, 128.41, 118.48, 112.75, 29.53, 12.88; ESIMS ( $m/z$ ) 180  $[\text{M}+\text{Na}]^+$ ; elemental analysis cal. for  $\text{C}_{11}\text{H}_{11}\text{N}$ ; C 84.04, H 7.05, N 8.91.

**Z-2-(4-Fluorobenzylidene) butanenitrile (2b):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ) :  $\delta$  7.74-7.67 (m, 2H ), 7.13-7.04 (m, 2H), 6.84 (s, Vinylic-H, for *E* isomer it appear at 7.11), 2.40 -2.47 (m, 2H), 1.25-1.29 (t,  $J = 7.6$  Hz, 3H) ;  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  141.11, 130.52, 130.40, 130.02, 129.98, 118.57, 115.96, 115.67, 112.62, 29.47, 12.90; ES-IMS ( $m/z$ ) 198  $[\text{M}+\text{Na}]^+$ ; elemental analysis cal. for  $\text{C}_{11}\text{H}_{10}\text{NF}$ , C 75.4; H 5.75; N 7.99.

**Z-2-( 4-Chlorobenzylidene) butanenitrile (3b):** Colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ) :  $\delta$  7.63-7.65 (d,  $J = 8.1$  Hz, 2H ), 7.36-7.38 (d,  $J = 8.1$  Hz, 2H), 6.83 (s, Vinylic-H, for *E* isomer it appear at 7.10), 2.41-2.47 ( m, 2H), 1.25-1.29 (t,  $J = 8.06$  Hz, 3H);  $^{13}\text{C}$  NMR ( 75MHz,  $\text{CDCl}_3$ ):  $\delta$

140.94, 135.54, 132.16, 129.66, 128.90, 118.34, 113.54, 29.46, 12.79; ESIMS ( $m/z$ ) 214  $[\text{M}+\text{Na}]^+$ ; elemental analysis cal. for  $\text{C}_{11}\text{H}_{10}\text{NCl}$ , C 68.93; H 5.26; N 7.31.

**Z-2-(4-Methylbenzylidene) butanenitrile (4b):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( 300MHz,  $\text{CDCl}_3$ ) :  $\delta$  7.57-7.60 (d,  $J = 8.31$  Hz, 2H), 7.16-7.19 (t,  $J = 8.3$  Hz, 2H), 6.84 (s, Vinylic-H, for *E* isomer it appear at 7.06), 2.33-2.46 (m, 5H), 1.23-1.28 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  142.05, 139.75, 131.00, 129.31, 128.44, 118.39, 111.54, 29.53, 21.35, 13.00; ESIMS ( $m/z$ ) 194  $[\text{M}+\text{Na}]^+$ ; elemental analysis cal. for  $\text{C}_{12}\text{H}_{13}\text{N}$ , C 84.19; H 7.65; N 8.18.

**Z-2-(4-Methoxybenzylidene) butanenitrile (5b):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ):  $\delta$  7.65-7.67 (d,  $J = 8.69$  Hz, 1H), 7.21-7.25 (d,  $J = 8.6$  Hz, 1H), 7.21-7.25 (d,  $J = 8.7$  Hz, 2H), 6.79 (s, Vinylic-H; for *E* isomer it appear at 7.07), 3.82 (s, 3H), 2.40-2.42 (m, 2H), 1.23-1.27 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  141.91, 130.21, 126.56, 119.04, 114.14, 109.93,55.24, 29.59, 13.21; ESIMS ( $m/z$ ) 188  $[\text{M}+\text{Na}]^+$ ; elemental analysis cal. for  $\text{C}_{12}\text{H}_{13}\text{NO}$ , C 76.98; H 7.00; N 7.48.

**(Z)-2-cyano-3-phenyl allylacetate (1d):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80-7.69 (m, 2H), 7.46-7.34 (m, 3H), 7.18 (s, 1H), 4.78 (s, 2H), 2.12 (s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$ 170.18, 147.26, 132.39, 131.86, 131.02, 129.05, 128.84, 105.66, 65.14, 20.64; ESIMS ( $m/z$ ) 224  $[\text{M}+\text{Na}]^+$ ; elemental analysis cal. for  $\text{C}_{12}\text{H}_{10}\text{NO}_2\text{F}$ , C 65.75; H 4.60; N 6.39.

**(Z)-2-cyano-3-(4-fluorophenyl) allylacetate (2d):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  7.83-7.74 (m, 2H), 7.16 (s, 1H), 7.14-7.08 (m, 2H) , 4.77 (s, 1H), 2.13 (s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  170.19, 165.61, 162.28, 145.92, 131.35, 131.23, 128.75, 128.69, 117.06, 116.24, 115.95, 105.39, 105.39, 65.04, 20.62; ESIMS ( $m/z$ ) 258  $[\text{M}+\text{K}]^+$ ; Elemental analysis cal. for  $\text{C}_{12}\text{H}_{11}\text{NO}_2$ , C 71.63; H 5.51; N 6.96.

**(Z)-3-(4-chlorophenyl)-2-cyano allylacetate (3d):** colourless liquid; IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 8.3$  Hz, 2H), 7.30 (d,  $J = 8.3$  Hz, 2H), 7.14 (s, 1H) , 4.77 (s, H), 2.13 (s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  170.13, 145.69, 137.02, 130.88, 130.30, 129.17, 128.26 116.86, 106.38, 64.93, 20.64; ESIMS ( $m/z$ )258  $[\text{M}+\text{Na}]^+$ ; Elemental analysis cal. for  $\text{C}_{12}\text{H}_{10}\text{NO}_2\text{Cl}$ , C 61.16; H 4.28; N 5.94.

**(Z)-2-cyano-3-(4-methoxyphenyl) allylacetate (4d):** colourless liquid, IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J = 8.3$  Hz, 2H), 7.22 (d,  $J = 8.3\text{Hz}$ , 2H), 7.13 (s, 1H) , 4.76 (s, 2H), 2.39 (s, 3H), 2.14 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  170.13, 145.69, 137.02, 130.88, 130.30, 129.17, 128.26 116.86, 106.38, 64.93, 20.64; ESIMS ( $m/z$ ) 254  $[\text{M}+\text{Na}]^+$ ; Elemental analysis cal. for  $\text{C}_{13}\text{H}_{13}\text{NO}_2$ , C 72.54; H 6.09; N 6.51.

**(Z)-2-cyano-3p-tolylallylacetate (5d):** yellow colour liquid; IR:  $\nu$  1711, 1599, 1514  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75 (d,  $J = 8.3$  Hz, 2H), 7.09 (s, 1H) ,6.91 (d,  $J = 8.3$  Hz, 2H), 4.74 (s, 2H), 3.84 (s, 3H), 2.12 (s, 3H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ ):  $\delta$  169.57, 161.72, 146.85, 131.28, 131.09, 125.28,114.37, 114.25, 102.65, 65.45,55.12, 20.63; ESIMS ( $m/z$ )254  $[\text{M}+\text{Na}]^+$ ; Elemental analysis cal. for  $\text{C}_{13}\text{H}_{13}\text{NO}_3$ , C 67.52; H 5.67; N 6.06.

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