Synthesis A. K. Khatana et al. Special Topic

A Highly Efficient NHC-Catalyzed Aerobic Oxidation of Aldehydes to Carboxylic Acids

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Dedicated to Dr. Srivari Chandrasekhar, IICT, Hyderabad, India on his 54th birthday

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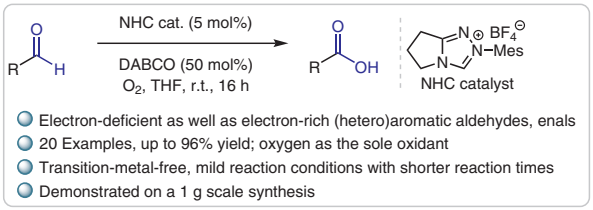

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Abstract An N-heterocyclic carbene (NHC) organocatalytic aerobic oxidation of aldehydes to the corresponding carboxylic acids is explored. Remarkably, this method allows for efficient conversion of different classes of aldehydes including highly challenging electron-rich aryl aldehydes, *ortho*-substituted aryl aldehydes, various heteroaromatic aldehydes and α,β-unsaturated aldehydes under mild reaction conditions. These substrates, under previously reported NHC-catalyzed methods, are typically unreactive or give poor yields, require high reaction temperatures and reaction times of several days.

Key words carboxylic acids, aldehydes, N-heterocyclic carbenes, aerobic oxidation, organocatalysis

Carboxylic acids are one of the most encountered functionalities in organic compounds used in pharmaceuticals, agrochemicals and industrial chemicals. In general, this class of compound is prepared via oxidation of the corresponding alcohol or aldehyde. Therefore, the oxidation of aldehydes to their carboxylic acid counterparts is a fundamentally significant organic manipulation with huge industrial application. Numerous metal-based oxidants have been developed, e.g., chromates, permanganates, perchlorates, peroxides, etc.[1] Oxidation reactions based on these hazardous oxidants utilize stoichiometric amounts of the oxidant and produce toxic by-products. The use of molecular oxygen as the oxidant offers several advantages over other reagents due to operational simplicity, higher atom economy, and produces water as the only by-product. Therefore, the development of catalytic, environmentally benign aerobic oxidation methods is of increasing interest and an attractive area of research in organic chemistry. Toward this objective, several metal-based catalytic aerobic oxidation methods have been developed.[2]

Metal-free organocatalysis has been extensively explored as an alternative mode of activation for a variety of transformations previously known to be catalyzed only by a metal complex.[3] This process offers several distinct advantages over metal-based approaches, including robustness in operation, ready availability, and improved environmental and economic aspects. Among all the organic-molecule-based catalysts, N-heterocyclic carbenes (NHCs) have evolved as the most promising catalysts for the oxidation of aldehydes to carboxylic acids.[4–6] To date, several methods using NHC catalysts have been developed. In 2009, Yoshida[7a] reported the oxidation of aldehydes using a sulfoxylalkyl-substituted imidazolium NHC catalyst. This was followed by independent reports from the groups of Zhang[7b] and Nair[7c] using CO_2 as the oxidant. In contrast to the reports of Zhang and Nair, Bode and Chiang proposed O_2 as the actual oxidant, and not CO_2, under their conditions.[8] In 2013, Fu reported an abnormal bis-NHC-mediated oxidation.[9] In spite of the remarkable progress realized in these reports, the methods suffer from one or more limitations such as limited substrate scope [primarily suitable for activated electron-deficient (hetero)aryl aldehydes], require reaction times of several days and/or higher temperatures. In a more recent publication, Blechert described the oxidation of a variety of electron-rich aryl aldehydes (along with other aldehydes) having *para*/*meta*-benzylic hydroxy functionality.[10] However, a more electron-rich *para*-hydroxybenzaldehyde required several days and a higher catalyst loading. In short, there is an urgent need for an efficient, metal-free catalytic method for challenging substrates like *ortho*-sub-

stituted aryl aldehydes, highly electron-rich aryl aldehydes (e.g., methoxybenzaldehydes) and indole-3-carboxaldehydes. Herein, we a report a highly efficient triazolium NHC-catalyzed aerobic oxidation of aryl aldehydes and enals at room temperature employing a much shorter reaction time.[11]

Experimentally, we set out to optimize the reaction conditions using benzaldehyde as a model substrate under an oxygen atmosphere and the key results are summarized in Table 1. In the absence of an NHC catalyst, no formation of product **2a** was observed (entry 1). Imidazolium NHC precatalysts **A**–**C** (Figure 1), with either *N*-isopropyl and *N*-Mes substituents, produced the desired acid **2a** in poor yields in the presence of DABCO as the base and THF as the solvent (entries 2–4). Thiazolium precatalyst **D** was not suitable for this reaction (entry 5).

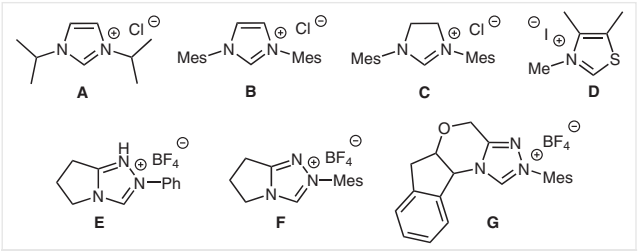
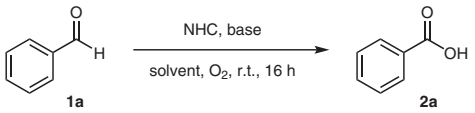


Figure 1 Catalysts **A**–**G**

Table 1 Optimization of the Reaction Conditions[a]



Entry	Catalyst	Base	Solvent	Yield (%)[b]
1	–	DABCO	THF	–
2	**A**	DABCO	THF	<5
3	**B**	DABCO	THF	16
4	**C**	DABCO	THF	25
5	**D**	DABCO	THF	<5
6	**E**	DABCO	THF	32
7	**F**	**DABCO**	**THF**	**92**
8	**G**	DABCO	THF	94
9	**F**	DBU	THF	36
10	**F**	Cs_2CO_3	THF	–
11	**F**	K_2CO_3	THF	–
12	**F**	*t*-BuOK	THF	–
13	**F**	DABCO	DMF	–
14	**F**	DABCO	DMSO	–
15	**F**	DABCO	CH_2Cl_2	–
16	**F**	DABCO	toluene	73
17	**F**	DABCO	MeCN	–
18[c]	**F**	DABCO	THF	93
19[d]	**F**	DABCO	THF	89
20[e]	**F**	DABCO	THF	72
21[f]	**F**	DABCO	THF	54
22[g]	**F**	DABCO	THF	76

[a] Reaction conditions: **1a** (0.5 mmol), catalyst **A**–**F** (5 mol%), base (50 mol%), O_2, solvent (3.0 mL), r.t.; unless otherwise specified.
[b] Yield of isolated product **2a**.
[c] 10 mol% of **F** was used.
[d] Reaction performed at 50 °C.
[e] 2 mol% of **F** was used.
[f] 1 mol% of **F** was used.
[g] Reaction under an air atmosphere.

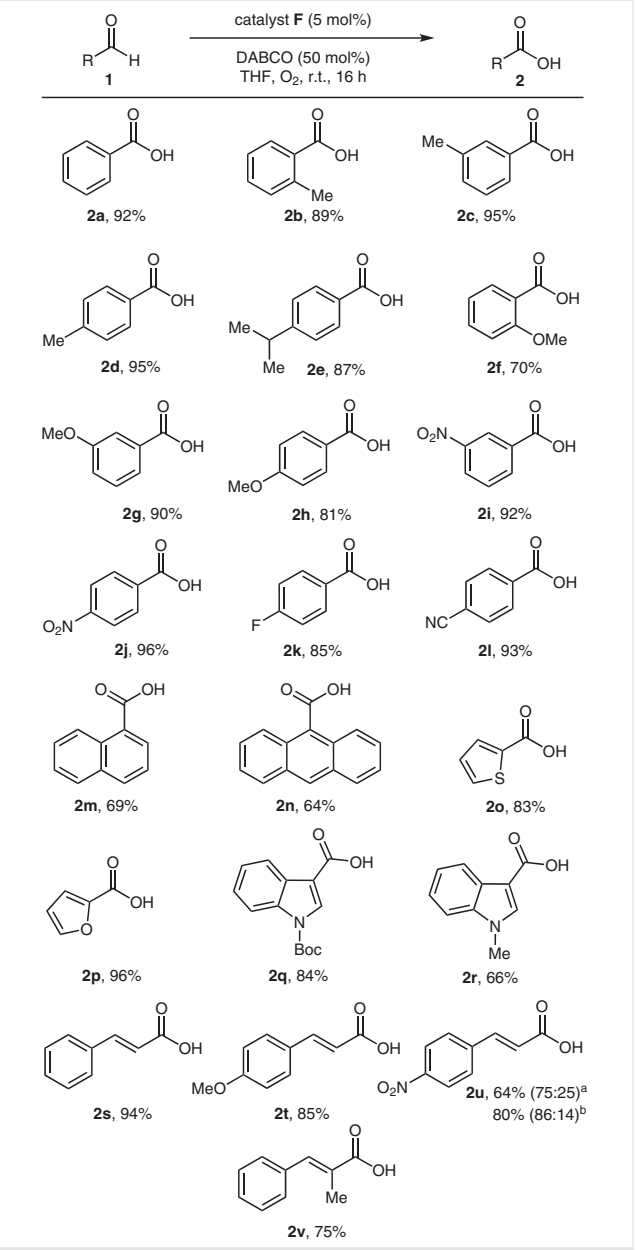
We next examined triazolium NHCs. Pyrrolidinone-derived precatalyst **E** with an *N*-phenyl substituent gave the desired product in a slightly improved yield of 32% (Table 1, entry 6). Replacing the *N*-phenyl group on this precatalyst with a more electron-rich *N*-Mes group (precatalyst **F**) had a dramatic influence on the conversion and the product **2a** could be isolated in an excellent yield of 92% (entry 7). The use of aminoindanol-based precatalyst **G** produced a comparable result (entry 8). Taking the cost, availability and atom economy into consideration, the precatalyst **F** was utilized further for the optimization study. Different bases such as DBU, Cs_2CO_3, K_2CO_3 and *t*-BuOK in the presence of precatalyst **F** in THF were not effective and led to either poor or no product formation (entries 9–12). With precatalyst **F** as the optimum NHC catalyst and DABCO as the base, we also investigated the solvent effect. Among all the other solvents screened, the desired product was only formed in toluene with a reduced yield of 73% (entries 13–17). A higher catalyst loading or an elevated reaction temperature had no noticeable improvement on the reaction yield (entries 18 and 19). Lower catalyst loadings resulted in reduced yields of product **2a** (entries 20 and 21), whilst the oxidation under an air atmosphere gave acid **2a** in a lower 76% yield (entry 22).

With optimized reaction conditions in hand (Table 1, entry 7), the substrate scope was investigated (Scheme 1). To our delight, even highly electron-rich aryl aldehydes afforded the desired products **2b**–**h** in good to excellent yields. A clear effect of the substitution pattern was observed. The *meta*- and *para*-substituted aryl aldehydes performed better than the corresponding *ortho*-substituted aldehydes (**2b** vs **2c** and **2d**; **2f** vs **2g** and **2h**). Electron-deficient aryl aldehydes also produced the corresponding carboxylic acids **2i**–**l** in good to excellent yields. Other aryl aldehydes such as 1-naphthaldehyde and anthracene-9-carboxaldehyde were well tolerated under the optimized conditions giving the products **2m** and **2n**, respectively, in good yields. Heteroaryl aldehydes were also found to be suitable substrates for this methodology leading to the corresponding acids **2o**–**r**. It is worth mentioning here that we were initially interested in preparing indole-3-carboxylic

acids (**2q** and **2r**, which are highly useful synthons) before embarking on this study, with most of the NHC-catalyzed protocols reported in the literature failing to produce a satisfactory result. We also examined the generality of several enals under our conditions. Neutral or electron-rich aryl substituents at the β-position of the enals produced the products **2s** and **2t** in excellent yields, whereas the presence of an electron-withdrawing substituent gave the product **2u** in good yield, but as a mixture with the corresponding saturated analogue in a 75:25 ratio. For this substrate, the use of catalyst **G** under similar reaction conditions slightly improved the yield and the ratio of the desired product (80% yield, 86:14). An enal substituted at the α-position also worked well affording acid **2v** in 75% yield. Even though partial conversion into the corresponding acid was observed with an aliphatic aldehyde (1-pentanal) and a β-alkyl-substituted enal (crotonaldehyde), the reaction was not clean, and the product could not be isolated in pure form (inseparable mixtures containing an unidentified impurity).

We next examined the reaction on a 1 grams scale using benzaldehyde. With 2 mol% and 5 mol% of catalyst loading, the expected product **2a** was obtained in 71% and 87% yield, respectively, over a reaction time of 24 hours.

In conclusion, we have developed a highly efficient triazolium-NHC-catalyzed method for the aerobic oxidation of aldehydes to the corresponding carboxylic acids under mild conditions in a short reaction time. More significantly, this method is suitable for several classes of challenging aldehydes such as *ortho*-substituted aryl aldehydes, highly electron-rich aryl aldehydes and indole-3-carboxaldehydes. We have also demonstrated this method for a gram-scale synthesis.



Scheme 1 Substrate scope of aldehydes **1**. *Reagents and conditions*: **1** (0.5 mmol), precatalyst **F** (5 mol%), DABCO (50 mol%), O_2, THF (3.0 mL), r.t., 16 h; unless otherwise specified. Yields are those of isolated products **2**. [a] Ratio of **2u** and its saturated analogue. [b] Precatalyst **G** was employed; ratio of **2u** and its saturated analogue.

Unless otherwise stated, all reactions were performed under an O_2 atmosphere. THF was distilled from Na using benzophenone as indicator. All aldehydes are commercially available and were used as supplied. TLC was carried out on precoated plates (Merck silica gel 60, F_{254}), and the spots were visualized with UV light or by dipping in PMA/$KMnO_4$ solution and charring the plates. ^1H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer using $CDCl_3$ or DMSO-d_6 as the solvent. The ^1H NMR data of all the isolated products were in agreement with those reported previously in the literature.

Oxidation; General Procedure

To a dry, two-neck 25 mL round-bottom flask equipped with a magnetic stir bar was added NHC catalyst **F** (0.025 mmol) and aldehyde **1** (0.5 mmol). The reaction vessel was charged with anhydrous THF (3 mL), followed by flushing with O_2 gas. DABCO (0.25 mmol) was added and the flask was again flushed with O_2 gas. The reaction mixture was stirred for 16 h at r.t. under an O_2 atmosphere (1 atm, O_2 balloon). After completion of the reaction, as monitored by TLC, the mixture was diluted with EtOAc (10 mL) and aqueous 1.0 M NaOH solution was added. The aqueous layer was separated, washed with EtOAc (10 mL) and acidified using 3.0 M aqueous HCl solution (10 ml). This aqueous layer was extracted with EtOAc (10 mL) twice and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the pure desired product.

Benzoic Acid (2a)[12a]

Pale yellow solid; yield: 56 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17–8.10 (m, 2 H, Ar-H), 7.66–7.59 (m, 1 H, Ar-H), 7.52–7.45 (m, 2 H, Ar-H).

2-Methylbenzoic Acid (2b)[12b]

Pale yellow solid; yield: 60 mg (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.45 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.28 (t, *J* = 7.2 Hz, 2 H, Ar-H), 2.67 (s, 3 H, CH_3).

3-Methylbenzoic Acid (2c)[12c]

Pale yellow solid; yield: 65 mg (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.04 (br s, 1 H, COOH), 7.95–7.93 (m, 2 H, Ar-H), 7.43 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.37 (t, *J* = 8.0 Hz, 1 H, Ar-H), 2.43 (s, 3 H, CH_3).

4-Methylbenzoic Acid (2d)[12a]

Pale yellow solid; yield: 65 mg (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.28 (d, *J* = 8.0 Hz, 2 H, Ar-H), 2.44 (s, 3 H, CH_3).

4-Isopropylbenzoic Acid (2e)[2a]

Off-white solid; yield: 71 mg (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.34 (d, *J* = 8.0 Hz, 2 H, Ar-H), 2.99 (sept, *J* = 7.2 Hz, 1 H, Ar-CH), 1.29 [d, *J* = 7.2 Hz, 6 H, $(CH_3)_2$].

2-Methoxybenzoic Acid (2f)[12a]

Pale yellow solid; yield: 53 mg (70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H, Ar-H), 7.57–7.52 (m, 1 H, Ar-H), 7.12–7.03 (m, 2 H, Ar-H), 4.05 (s, 3 H, CH_3).

3-Methoxybenzoic Acid (2g)[12a]

Pale yellow solid; yield: 68 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.64–7.63 (m, 1 H, Ar-H), 7.39 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.18–7.15 (m, 1 H, Ar-H), 3.87 (s, 3 H, CH_3).

4-Methoxybenzoic Acid (2h)[12a]

Pale yellow solid; yield: 62 mg (81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.58 (br s, 1 H, COOH), 7.89 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.00 (d, *J* = 8.8 Hz, 2 H, Ar-H), 3.82 (s, 3 H, CH_3).

3-Nitrobenzoic Acid (2i)[12a]

Pale yellow solid; yield: 77 mg (92%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.59 (s, 1 H, Ar-H), 8.45 (d, *J* = 8.0 Hz, 1 H, Ar-H), 8.33 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.80 (t, *J* = 8.0 Hz, 1 H, Ar-H).

4-Nitrobenzoic Acid (2j)[12a]

Light yellow solid; yield: 80 mg (96%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.32 (d, *J* = 8.8 Hz, 2 H, Ar-H), 8.17 (d, *J* = 8.8 Hz, 2 H, Ar-H).

4-Fluorobenzoic Acid (2k)[2a]

White solid; yield: 60 mg (85%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.00 (br s, 1 H, COOH), 8.04–7.95 (m, 2 H, Ar-H), 7.30 (t, *J* = 8.8 Hz, 2 H, Ar-H).

4-Cyanobenzoic Acid (2l)[12a]

Pale yellow solid; yield: 68 mg (93%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.52 (br s, 1 H, COOH), 8.07 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.96 (d, *J* = 8.0 Hz, 2 H, Ar-H).

1-Napthoic Acid (2m)[2a]

Light yellow solid; yield: 59 mg (69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.12 (d, *J* = 8.8 Hz, 1 H, Ar-H), 8.44 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1 H, Ar-H), 8.11 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.93 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.72–7.64 (m, 1 H, Ar-H), 7.62–7.53 (m, 2 H, Ar-H).

Anthracene-9-carboxylic Acid (2n)[12d]

Yellow solid; yield: 71 mg (64%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.90 (br s, 1 H, COOH), 8.72 (s, 1 H, Ar-H), 8.15 (d, *J* = 8.4 Hz, 2 H, Ar-H), 8.08 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.67–7.53 (m, 4 H, Ar-H).

Thiophene-2-carboxylic Acid (2o)[2a]

White solid; yield: 53 mg (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (dd, J_1 = 3.6 Hz, J_2 = 1.2 Hz, 1 H, Ar-H), 7.65 (dd, J_1 = 5.2 Hz, J_2 = 1.2 Hz, 1 H, Ar-H), 7.15 (dd, J_1 = 5.2 Hz, J_2 = 1.2 Hz, 1 H, Ar-H).

Furoic Acid (2p)[2a]

White solid; yield: 54 mg (96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (br s, 1 H, COOH), 7.64 (s, 1 H, Ar-H), 7.33 (d, *J* = 3.6 Hz, 1 H, Ar-H), 6.56 (dd, J_1 = 3.6 Hz, J_2 = 1.6 Hz, 1 H, Ar-H).

1-(*tert*-Butoxycarbonyl)-1*H*-indole-3-carboxylic Acid (2q)[12e]

White solid; yield: 110 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (s, 1 H, Ar-H), 8.25–8.16 (m, 2 H, Ar-H), 7.44–7.33 (m, 2 H, Ar-H), 1.71 (s, 9 H, Boc).

***N*-Methyl-1*H*-indole-3-carboxylic Acid (2r)**[12f]

Light brown solid; yield: 63 mg (66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25–8.21 (m, 1 H, Ar-H), 7.89 (s, 1 H, Ar-H), 7.40–7.30 (m, 3 H, Ar-H), 3.87 (s, 3 H, CH_3).

***trans*-Cinnamic Acid (2s)**[12g]

White solid; yield: 70 mg (94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.10 (br s, 1 H, COOH), 7.71 (d, *J* = 16 Hz, 1 H, Alkene-H), 7.51–7.41 (m, 2 H, Ar-H), 7.37–7.27 (m, 3 H, Ar-H), 6.37 (d, *J* = 16 Hz, 1 H, Alkene-H).

***trans*-4-Methoxycinnamic Acid (2t)**[12g]

Off white solid; yield: 76 mg (85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 16 Hz, 1 H, Alkene-H), 7.50 (d, *J* = 8.8 Hz, 2 H, Ar-H), 6.92 (d, *J* = 8.8 Hz, 2 H, Ar-H), 6.31 (d, *J* = 16 Hz, 1 H, Alkene-H), 3.85 (s, 3 H, CH_3).

***trans*-4-Nitrocinnamic Acid (2u)**[12g]

Off white solid; yield: 78 mg (80%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.50 (br s, 1 H, COOH), 8.22 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.96 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.68 (d, *J* = 16 Hz, 1 H, Alkene-H), 6.73 (d, *J* = 16 Hz, 1 H, Alkene-H).

(*E*)-α-Methylcinnamic Acid (2v)[12h]

White solid; yield: 61 mg (75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.60 (br s, 1 H, COOH), 7.75 (d, *J* = 1.2 Hz, 1 H, Alkene-H), 7.36–7.21 (m, 5 H, Ar-H), 2.05 (d, *J* = 1.2 Hz, 3 H, α-CH_3).

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610069.

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