Mild aerobic oxidation of alcohols catalysed by $Fe_2(SO_4)_3/4$ -OH-TEMPO/NaNO₂ Xiang-Jun Shi, Jie Qian, Fan-Fan Tan and Chuan-Ming Yu*

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An environmentally friendly catalytic system of $Fe_2(SO_4)_3/4$ -OH-TEMPO/NaNO₂ has been developed for aerobic oxidation of alcohols to aldehydes and ketones. The catalytic system allowed efficient and selective oxidation of a wide range of alcohols using oxygen at 1 atmospheric pressure and room temperature. 100% selectivity and excellent conversion rates were observed for benzylic alcohols and cinnamyl alcohol.

Keywords: alcohols, TEMPO, iron salts, aerobic oxidation, oxygen

Selective oxidation of alcohols to the corresponding aldehydes or ketones is important in chemical syntheses of pharmaceuticals, fragrances food additives and more.1-3 Traditionally, the alcohol oxidation requires addition of a stoichiometric amount of inorganic oxidants such as CrO₃,⁴ KMnO₄ and MnO₂,⁵ which generate hazardous by-products and cause environmental problems, especially when the reaction is carried out on an industrial scale. To address this issue, many research groups have been looking for an efficient, high yield and selective catalyst system for the oxidation of alcohols to the corresponding carbonyl compounds. In 1975, Cella⁶ and Ganern⁷ discovered that 2,2,6,6-tetramethyl-piperidyl-1-oxy (TEMPO) could be used in the alcohol oxidation. Later, numerous TEMPOrelated systems have been reported for the alcohol oxidation. Among these, the catalytic systems using both transition metals and TEMPO are of particular interest. Sheldon et al.8 developed a RuCl₂(PPh₃)₃/TEMPO catalytic system for efficient aerobic oxidation of primary and secondary alcohols. Stahl et al.9 reported a CuI/TEMPO catalyst system that could oxidise primary alcohols under an ambient atmosphere of air at room temperature. Recently, Liang et al.¹⁰ reported the first use of FeCl₃/TEMPO/NaNO₂ as a catalytic system and achieved quantitative conversion in alcohol oxidations. This cheap and environmentally friendly iron/TEMPO catalytic system has quickly attracted a lot of attention. For further optimisation of the FeCl₃/TEMPO/NaNO₂ catalytic system, Liu et al.¹¹ screened a variety of 4-substituted-TEMPO examples and discovered that among these, 4-acetamido-TEMPO was the most effective one, but 4-OH-TEMPO was the least active one and showed only a 49% conversion rate. Wang et al.12 used silica gel to enhance the catalytic activity of various iron salt/TEMPO systems; catalyst containing FeCl₃ showed good activity, but $Fe_2(SO_4)_3$ was not effective and yielded only a 8% conversion rate. Ma et al.^{13,14} developed a Fe(NO₃)₃/TEMPO catalytic system to oxidise alcohols, including allenols and propargyl alcohols, under aerobic conditions at room temperature; interestingly, a catalytic amount of chloride ion was reported to be able to expedite the reaction, so sodium chloride was added to provide an inorganic halide ligand. Furthermore, Aoyama et al.¹⁵ reported a catalytic system using Fe(NO₃)₃ in a nonpolar solvent and 4-hydroxy-TEMPO-NaCl loaded SiO₂ which could be recovered by filtration and reused; the oxidation of various alcohols proceeded smoothly at room temperature. Zheng¹⁶ filed a patent for citronellal preparation through citronellol oxidisation using catalytic systems containing TEMPO or its derivatives, iron-, cuprous- or tin-containing salts, various ligands and bases.

The iron/TEMPO catalytic system showed early promise as an inexpensive and environmentally friendly synthetic method for alcohol oxidation. We were interested in optimising the iron salt/TEMPO catalytic system to increase its selectivity and efficiency, so the method could be used on an industrial scale. After screening various combinations of iron salts and TEMPO derivatives, we discovered that a novel fourcomponent oxidation system consisting of 1 atm O_2 , $Fe_2(SO_4)_3$, 4-OH-TEMPO(TMHPO) and NaNO₂ could oxidise most benzylic alcohols and cinnamyl alcohol with 100% selectivity and excellent yields. We now report the development of our four-component oxidation system, its reaction mechanism, and the oxidation results using various alcohols.

Results and discussion

Oxidation of 4-methylbenzyl alcohol was chosen as a model reaction to determine the optimal reaction conditions. First, we screened various iron salts in the presence of 1 atm O₂, 5 mol% TMHPO, 5 mol% NaNO₂ at room temperature. As shown in Table 1 in the presence of the iron salts, the alcohol was converted to 4-methylbenzaldehyde with 100% selectivity (Table 1, entries 1-5), and no acid formation was observed. Among these iron salts, $Fe_2(SO_4)_3$ was the most efficient catalyst (Table 1, entry 3) which converted the alcohol to the aldehyde in 3h with 98.3% alcohol conversion rate. FeSO₄•7H₂O (Table 1, entry 4) achieved 93.4% conversion rate in 6h. The conversion rates obtained in the presence of FeCl₃•6H₂O, Fe(NO₃)₃•9H₂O, FeCl₂•4H₂O were significantly lower (69-78%, Table 1) and required longer reaction time. Also, these results showed that Fe^{3+} salts ($Fe_2(SO_4)_3$ or $FeCl_3 \bullet 6H_2O$) had a better catalytic activity than the corresponding Fe²⁺ salts (FeSO₄•7H₂O or FeCl₂•4H₂O). Interestingly, the counterion of the iron salts also had some effect on the conversion rate. The sulfate ion was more effective in this catalytic system than

 Table 1
 Oxidation of 4-methylbenzyl alcohol in the presence of various iron salts

Iron salt	Time/h	Select./% ^b	Conv./% ^b
FeCl ₃ •6H ₂ O	12	100	77.5
FeCl ₂ •4H ₂ O	24	100	70.2
Fe ₂ (SO ₄) ₃	3	100	98.3
FeSO ₄ •7H ₂ O	6	100	93.4
Fe(NO ₃) ₃ •9H ₂ O	12	100	69.1
Fe ₂ (SO₄) ₃ +0.1%NaCl	3	100	93.0
Fe ₂ (SO ₄) ₃ +1.0%NaCl	3	100	91.3
Fe ₂ (SO ₄) ₃ +15%NaCl	3	100	79.8
	$\label{eq:result} Iron salt \\ FeCl_3 {}^{\bullet}6H_2O \\ FeCl_2 {}^{\bullet}4H_2O \\ Fe_2(SO_4)_3 \\ FeSO_4 {}^{\bullet}7H_2O \\ Fe(NO_3)_3 {}^{\bullet}9H_2O \\ Fe_2(SO_4)_3 {}^{\bullet}.0.1\% NaCl \\ Fe_2(SO_4)_3 {}^{\bullet}1.0\% NaCl \\ Fe_2(SO_4)_3 {}^{\bullet}.15\% NaCl \\ Fe_2(SO_4)_3 {}^{\bullet}.15\% NaCl \\ \end{array}$	$\begin{tabular}{ c c c c } \hline Iron salt & Time/h \\ \hline FeCI_3 \bullet 6H_2O & 12 \\ FeCI_2 \bullet 4H_2O & 24 \\ Fe_2(SO_4)_3 & 3 \\ FeSO_4 \bullet 7H_2O & 6 \\ Fe(NO_3)_3 \bullet 9H_2O & 12 \\ \hline Fe_2(SO_4)_3 \bullet 0.1\% NaCl & 3 \\ Fe_2(SO_4)_3 + 1.0\% NaCl & 3 \\ Fe_2(SO_4)_3 + 15\% NaCl & 3 \\ \hline \end{array}$	$\begin{tabular}{ c c c c c } \hline Iron salt & Time/h & Select./\%^b \\ \hline FeCl_3 \bullet 6H_2O & 12 & 100 \\ FeCl_2 \bullet 4H_2O & 24 & 100 \\ Fe_2(SO_4)_3 & 3 & 100 \\ FeSO_4 \bullet 7H_2O & 6 & 100 \\ Fe(NO_3)_3 \bullet 9H_2O & 12 & 100 \\ Fe_2(SO_4)_3 + 0.1\%NaCl & 3 & 100 \\ Fe_2(SO_4)_3 + 1.0\%NaCl & 3 & 100 \\ Fe_2(SO_4)_3 + 15\%NaCl & 3 & 100 \\ \hline \hline \end{array}$

^aReaction conditions: 5 mmol 4-methylbenzyl alcohol, 5 mol% iron salt, 5 mol% TMHPO, 5 mol% NaNO₂, 5 mL acetonitrile, 10 mL water, 1 atm O₂, room temperature.

^bConversion and selectivity are based on gas chromatography with area normalisation.

 $^{\rm c}\text{Fe}_2(SO_4)_3$ was analytical grade, the content of chlorine ion was 0.003%.

^d 0.1% of the mass of $Fe_2(SO_4)_3$. ^e 1% of the mass of $Fe_2(SO_4)_3$. ^f 15% of the mass of $Fe_2(SO_4)_3$.

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 Table 2
 Influence of the co-solvent/water mixture on the oxidation of 4-methylbenzyl alcohol

Entry ^a	Solvent mixture (v/v)	Time/h	Select./%	^b Conv./% ^b
1	Acetonitrile	12		Trace
2	Acetonitrile/water (1/2)	4	100	100
3	Acetonitrile/water (2/1)	4	100	91.4
4	DMF/water(1/2)	8	100	89.3
5	DMF/water(2/1)	24	100	76.2
6	THF/water(1/2)	9	100	79.3
7	THF/water(2/1)	24	100	92.2
8	Acetone/water (1/2)	24	100	63.8
9	Acetone/water (2/1)	24	100	65.0

^aReaction conditions: 5 mmol 4-methylbenzyl alcohol, 5 mol% $Fe_2(SO_4)_3$, 5 mol% TMHPO, 5 mol% NaNO₂, 1 atm O₂, room temperature.

^bConversion and selectivity are based on gas chromatography with area normalisation.

chloride ion and nitrate ion. Ma and Aoyama^{13–15} reported that chloride ion could promote the catalytic activity, but in our catalytic system addition of chloride ion decreased the conversion rate (Table 1, entries 6–8).

The type of solvent was reported to have a great influence on the oxidation of alcohols when a transition metal catalytic system was used.¹⁷⁻¹⁹ In our early trials, we chose acetonitrile as the solvent because of its excellent dissolution properties to most organics (Table 2, entry 1). However the alcohol substrate remained unreactive probably due to the poor solubility of $Fe_2(SO_4)_3$ in acetonitrile. Therefore, a mixture of acetonitrile/ water was employed in the reaction. As shown in Table 2, 100% conversion of the alcohol to 4-methylbenzaldehyde with 100% selectivity was achieved in a 1:2 (v/v) acetonitrile/water solvent mixture after 4h reaction (Table 2, entry 2). Also, increasing the percentage of acetonitrile in the solvent led to a slight decrease of conversion (Table 2, entry 3). These indicated that water might play a key role in improving the catalytic activity. The addition of water might help by forming a more homogeneous reaction system which could accelerate the oxidation reaction. We also tested three other water-miscible solvent mixtures (DMF/water, THF/water and acetone/water solvent mixture) at a ratio 1/2 and 2/1 (Table 2, entries 4–9), and all the conditions gave 4-methylbenzaldehyde in moderate conversion.

The optimised reaction conditions were applied to the oxidation of a variety of alcohols in order to explore the versatility of this aerobic catalytic system. As revealed in Table 3, most benzylic alcohols were converted into the corresponding aldehydes or ketones in high yield and excellent selectivity (Table 3, entries 1-7, 9, 10, 17-19 and 21). However, the electronic property of the substituents on the benzene ring had an apparent effect; benzylic alcohols with electron-donating substituents (Table 3, entries 2-5) were converted to the corresponding aldehydes in shorter time with higher conversion rate, in comparison with those bearing electron-withdrawing substituents (Table 3, entries 6-11). In the case of benzyl alcohols containing the electron-donating methoxy group (Table 3, entries 3-5), the substitution position affected the reaction rate; the o- and p- substituted compounds (Table 3, entries 3) and 5) reacted faster than that of the m-substituted one (Table 3, entry 4). Perhaps, in this case, the electronic effects are dominant over the steric effects. In the case of benzyl alcohols substituted with the electron-withdrawing fluoride group (Table 3, entries 6-8), the *m*- and *p*-substituted compounds showed much better results than the o-substituted example. This might be due to the effect of the intermolecular hydrogen bonding between the fluoride atom at o-position and the hydroxyl group. Secondary benzylic alcohols could be converted to the corresponding ketones (Table 3, entries 17–21), but 1-(2-chlorophenyl)ethanol gave only a 30% isolated yield

Table 3 Catalytic aerobic oxidation of alcohols in the presence of 4-OH-TEMPO, Fe₂(SO₄)₃ and NaNO₂^a

OН

			TMHPO, Fe	TMHPO, Fe ₂ (SO ₄) ₃ , NaNO ₂			
		R ¹	R^2 1 atm O ₂ ,	CH ₃ CN/H ₂ O, rt	$R^1 R^2$		
		а			b		
Entry	R ¹	R ²	Products	Time/h	Conv./% ^b	Select./% ^b	Yield/%℃
1	C_6H_5	Н	1b	8	98.8	100	89
2	4-CH ₃ C ₆ H ₄	Н	2b	4	100	100	93
3	4-CH ₃ OC ₆ H ₄	Н	3b	3	100	100	95
4	3- CH ₃ OC ₆ H ₄	Н	4b	8	100	100	96
5	2- CH₃OC ₆ H₄	Н	5b	5	100	100	93
6 ^d	4-FC ₆ H ₄	Н	6b	12	100	100	95
7 ^d	3- FC ₆ H₄	Н	7b	12	91.8	100	85
8 ^d	2- FC ₆ H ₄	Н	8b	24	53.1	100	45
9 ^d	4-CIC ₆ H ₄	Н	9b	12	98.2	100	93
10 ^d	$4-BrC_6H_4$	Н	10b	12	97.2	100	92
11 ^d	$4-NO_2C_6H_4$	Н	11b	12	46.2	100	40
12	C ₆ H₅CH=CH	Н	12b	24	96.6	100	92
13 ^d	3-Pyridyl	Н	13b	24	32.9	100	21
14 ^d	2-Furyl	Н	14b	24	77.3	100	60
15 ^d	$C_6H_5CH_2$	Н	15b	24	12.7	50	-
16 ^d	Cyclohexanol		16b	24	42.7	100	30
17	4-CH ₃ C ₆ H ₄	CH₃	17b	3	100	100	95
18	4-CH ₃ OC ₆ H ₄	CH₃	18b	3	100	100	94
19	$4-FC_6H_4$	CH₃	19b	8	100	100	93
20	2-CIC ₆ H ₄	CH₃	20b	24	37.7	100	30
21 ^d	C_6H_5	C ₆ H ₅	21b	24	100	100	94

^aReaction conditions: 5 mmol alcohol, 5 mol% Fe₂(SO₄)₃, 5 mol% TMHPO, 5 mol% NaNO₂, 1 atm O₂, room temperature.

^b Conversion and selectivity are based on gas chromatography (GC) with area normalisation.

° isolated yield.

^d5 mmol alcohol, 8 mol% Fe₂(SO₄)₃, 8 mol% TMHPO, 10 mol% NaNO₂, 1 atm O₂, room temperature.



Scheme 1 Proposed mechanism for $Fe_2(SO_4)_3/4$ -OH-TEMPO/NaNO₂-catalysed aerobic oxidation of alcohols.

(Table 3, entry 20). This perhaps was also due to the intermolecular hydrogen bonding effect. Cinnamyl alcohol could be oxidised into cinnamaldehyde smoothly in 92% isolated yield (Table 3, entry 12). 2-Furan methanol was converted into 2-furaldehyde in good conversion (Table 3, entry 14), but 2-pyridine methanol only gave a low conversion rate (Table 3, entry 13). As shown in the Table 3, the aliphatic alcohols were less active than the benzylic alcohols. For example, phenylethanol showed a very low conversion rate and 50% selectivity (Table 3, entry 15), and cyclohexanol gave only a 30% yield of cyclohexanone (Table 3, entry 16).

On the basis of some literature data^{10,20} and the preliminary studies, the catalytic cycle was proposed as shown in Scheme 1. TMHPO first coupled with Fe(III) to give intermediate **I**, which then reacted with the alcohol to form intermediate **II**. Intermediate **II** might undergo β -H elimination to form intermediate (**III**) and then an intramolecular one-electron transfer occurred to generate the corresponding aldehyde, TMHPOH (**IV**) and Fe(II). TMHPOH (**IV**) and Fe(II) could be reoxidised by NO₂ to regenerate TMHPO and Fe(III). NaNO₂ could be a source of NO₂.

Conclusion

In conclusion, we have further explored the iron salts/TEMPO catalytic systems and developed a novel catalytic system using $Fe_2(SO_4)_3$ /TMHPO/NaNO₂ for aerobic oxidation. This novel four component oxidation system used oxygen as a clean oxidant and inexpensive $Fe_2(SO_4)_3$ /4-OH-TEMPO/NaNO₂ as catalyst, and has achieved high selectivity in alcohol oxidation at room temperature and high yield when benzylic alcohols and cinnamyl alcohols were used. These desirable features made the method attractive for potential industrial usage.

Experimental

All reagents were purchased from commercial sources and were used as received. ¹H NMR spectra were recorded on a Varian 400 MHz instrument using CDCl₃ as the solvent, and chemical shifts were expressed in parts per million (ppm) using TMS as an internal standard. GC analyses for determining the conversion and selectivity of the reactions were performed on an Agilent 6890N GC system equipped with a HP-5 column using N_2 as carrying gas. Melting points were determined with a Büchi B-540 capillary melting point apparatus.

The oxidation of alcohols was carried out under O_2 in a 50-mL two-necked, round-bottom flask equipped with a magnetic stirrer. Typically, $Fe_2(SO_4)_3$ (0.25 mmol) and TMHPO (0.25 mmol) were added to the flask, followed by 15 mL of a CH₃CN/H₂O (1:2) solvent mixture. After stirring for 5 min, the alcohol (5 mmol) was added, followed by NaNO₂ (0.25 mmol). The resulting mixture was stirred at room temperature and 1 atm pressure of oxygen. When the reactions were completed, the reaction mixture was transferred to a separating funnel and extracted with dichloromethane. The organic layer was dried over anhydrous Na₂SO₄ and concentrated and further purified by flash chromatography to give the desired product.

Benzaldehyde (**1b**): Colourless liquid; ¹H NMR (CDCl₃, 400 MHz): δ 10.00 (s, 1H), 7.88–7.84 (m, 2H), 7.64–7.59 (m, 1H), 7.52 (t, *J* = 8.0 Hz, 2H).

4-*Methylbenzaldehyde* (**2b**): Light yellow liquid; ¹H NMR (CDCl₃, 400 MHz): δ 9.93 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H) 2.43 (s, 3H).

4-Methoxybenzaldehyde (**3b**): Light yellow liquid; ¹H NMR (CDCl₃, 400 MHz): δ 9.86 (s, 1H), 7.84–7.79 (m, 2H), 7.01–6.96 (m, 2H) 3.88 (s, 3H).

3-Methoxybenzaldehyde (**4b**): Pale yellow oily liquid; ¹H NMR (CDCl₃, 400 MHz): δ 9.95 (s, 1H), 7.44–7.42 (m, 2H), 7.37 (d, J = 4.0 Hz, 1H), 7.16 (dt, J = 8.0, 4.0 Hz, 1H), 3.86 (s, 3H).

2-Methoxybenzaldehyde (**5b**): Pale yellow solid; m.p. 38–39 °C (lit.²¹ 37–39 °C); ¹H NMR (CDCl₃, 400 MHz): δ 10.44 (s, 1H), 7.81 (dd, J = 8.0, 4.0 Hz, 1H), 7.57–7.49 (m, 1H), 6.99 (dd, J = 16.0, 4.0 Hz, 2H), 3.92 (s, 3H).

4-*Fluorobenzaldehyde* (**6b**): Yellow liquid; ¹H NMR (CDCl₃, 400 MHz): δ 9.95 (s, 1H), 7.90 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 2H).

3-Fluorobenzaldehyde (**7b**): Yellow liquid; ¹H NMR (CDCl₃, 400 MHz): δ 9.98 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58–7.49 (m, 2H), 7.33 (td, *J* = 8.0, 4.0 Hz, 1H).

2-*Fluorobenzaldehyde* (**8b**): Light yellow liquid; ¹H NMR (CDCl₃, 400 MHz): δ 10.35 (s, 1H), 7.88–7.83 (m, 1H), 7.62–7.56 (m, 1H), 7.29–7.23 (m, 1H), 7.20–7.13 (m, 1H).

4-*Chlorobenzaldehyde* (**9b**): Pale yellow solid; m.p. 46–47 °C (lit.²¹ 45–48 °C); ¹H NMR (CDCl₃, 400 MHz): δ 9.96 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H).

4-Bromobenzaldehyde (10b): White solid; m.p. 56–58 °C (lit.²² 57 °C); 'H NMR (CDCl₃, 400 MHz): δ 9.95 (s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H).

4-Nitrobenzaldehyde (11b): White solid; m.p. 106–107 °C (lit.²¹ 104–106 °C); ¹H NMR (CDCl₃, 400 MHz): δ 10.15 (s, 1H), 8.39 (d, J = 8.0 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H).

Cinnamaldehyde (12b): Light yellow liquid; ¹H NMR (CDCl₃, 400 MHz): δ 9.68 (d, J = 8.0 Hz, 1H), 7.57–7.53 (m, 2H), 7.49–7.40 (m, 4H), 6.70 (dd, J = 16.0, 8.0 Hz, 1H).

3-Pyridinecarboxaldehyde (13b): Light yellow liquid; ¹H NMR (CDCl₃, 400 MHz): δ 10.11 (s, 1H), 9.07 (d, J = 2.0 Hz, 1H), 8.84 (dd, J = 8.0, 2.0 Hz, 1H), 8.17 (dt, J = 8.0, 4.0 Hz, 1H), 7.49 (dd, J = 8.0, 8.0 Hz, 1H).

Furan-2-carbaldehyde (**14b**): Yellow liquid; ¹H NMR (CDCl₃, 400 MHz): δ 9.64 (s, 1H), 7.72–7.65 (m, 1H), 7.29–7.21 (m, 1H), 6.63–6.56 (m, 1H).

Cyclohexanone (**16b**): Colourless liquid; ¹H NMR (CDCl₃, 400 MHz): δ 2.33 (t, *J* = 6.5 Hz, 4H), 1.90–1.82 (m, 4H), 1.72 (ddd, *J* = 8.7, 6.4, 4.4 Hz, 2H).

l-(*p*-*Tolyl*)*ethanone* (**17b**): Colourless liquid; ¹H NMR (CDCl₃, 400 MHz): δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.57 (s, 3H), 2.40 (s, 3H).

1-(4-Methoxyphenyl)ethanone (**18b**): White solid; m.p. 38–39 °C (lit.²³ 37–39 °C); ¹H NMR (CDCl₃, 400 MHz): δ 7.94–7.88 (m, 2H), 6.94–6.88 (m, 2H), 3.86 (s, 3H), 2.55 (s, 3H).

l-(*4-Fluorophenyl*)*ethanone* (**19b**): Colourless liquid; ¹H NMR (CDCl₃, 400 MHz): δ 8.00–7.94 (m, 2H), 7.25–6.95 (m, 2H), 2.59 (s, 3H).

1-(2-Chlorophenyl)ethanone (**20b**): Colourless liquid; ¹H NMR (CDCl₃, 400 MHz): δ 7.53 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.43–7.34 (m, 2H), 7.33–7.27 (m, 1H), 2.64 (s, 3H).

Benzophenone (**21b**): White solid; m.p. 48–49 °C (lit.²³ 48–49 °C); ¹H NMR (CDCl₃, 400 MHz): δ 7.80–7.77 (m, 4H), 7.59–7.54 (m, 2H), 7.46 (t, *J* = 8.0 Hz, 4H).

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