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Manganese triacetate as an efficient catalyst for bisperoxidation of styrenes

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A method was developed for the bisperoxidation of styrenes with tert-butyldihydroperoxide in the presence of a catalytic amount of manganese(III) acetate. It was shown that compounds of manganese in oxidation states 2, 4, and 7 also catalyze this reaction. Target [1,2-bis(tert-butyldiperox)ethyl]arenes were synthesized in yields from 46 to 75%.

Introduction

Due to the ready availability and high efficiency, organic peroxides have been widely used for more than half a century as radical polymerization initiators in the industrial synthesis, for example, of such polymers as polystyrene, polyvinyl chloride, polycarbonate, and high-pressure polyethylene. Organic peroxides are also used for the crosslinking of silicone, acrylonitrile-butadiene, and fluorinated rubbers. A wide variety of commercial monomers and their compositions demands a wide assortment of peroxides, the most well-known of which are organic hydroperoxides, dialkyl peroxides, diacyl peroxides, peroxy esters, peroxydicarbonates, peroxy carbonates, peracets, cyclic triperoxides, and geminalbishydroperoxides. In the past decades, organic peroxides have got attention from researchers in the fields of medicinal chemistry and pharmacology because these compounds, particularly oxonides and tetroxanes, were found to exhibit marked antimalarial, anthelmintic, and antitumor activities. Peroxides, particularly derivatives of lower aldehydes and ketones, are still attracting interest also as energy-rich compounds. For instance, the explosive power of triacetone triperoxide is comparable with that of trinitrotoluene.

Due to the tendency of peroxides to decompose, their high sensitivity to reducing agents and variable valence metal ions, and the ease of a large range of transformations accompanied by the O-O bond cleavage, the search for general approaches to the synthesis of peroxides and the selective synthesis of peroxides of the specified structure are difficult problems. The transition metal (Cu, Mn, Co)/hydroperoxide system was used for the first time by Kharasch in the synthesis of peroxides from alkenes, ketones, and tertiary amines more than six decades ago. Since that time, the research on and application of this peroxidation method were documented in a number of publications. The formation of peroxides was observed in various reactions of hydroperoxides catalyzed by metal salts and their complexes: copper, cobalt, and iron, dinuclear nickel complexes, palladium acetate, ruthenium(II)-bipyridine anchored montmorillonite, and metalloporphyrs. Peroxides were synthesized in high yields by the peroxidation of amines, amides, and lactams catalyzed by ruthenium salts. Examples of the synthesis of such compounds are limited by the tendency of peroxides to decompose in the presence of variable valence metals.

In the present study, we developed a new approach to the synthesis of vicinal bis(tert-butyldiperox) styrenes and tert-butyldihydroperoxide using manganese(III) acetate. Manganese(III) acetate is a strong oxidizer. This compound proved to be an efficient reagent in redox and free radical reactions accompanied by the C-C, C-O, and C-N bond formation. The combination of two oxidizing agents, Mn(OAc) and TBHP, imparts new properties to the system. These properties were used to oxidize alkenes at the allylic position to form enones. The known methods for the synthesis of vicinal bisperoxides from styrenes and TBHP are based on the use of palladium acetate, ruthenium(II) bipyridine anchored montmorillonite, dinuclear nickel complexes, and Mn(III) porphyrins. The drawback of the former two approaches, although they provide good yields (65-85% and 30-69%, respectively), is the use of expensive catalysts. In the third approach, the difficult-to-prepare catalyst is employed and, besides, the target bisperoxide is produced in a rather low yield (26%). The reactions with the use of iron(III) or manganese(III) porphyrins (Fe(III)/TDCIPP-OAc or Mn(III)/TDCIPP-OAc) give the target products with low yields.

In the present study, we found that styrenes are selectively peroxidized with high conversion in the reaction with TBHP and manganese(III) acetate to form vicinal bisperoxides ([1,2-bis(tert-butyldiperox)ethyl]arenes).

Results and discussion

Vicinal bisperoxides 2a-i (Scheme 1) were synthesized from styrenes 1a-i containing substituents of different nature.
In order to optimize the reaction conditions, we studied the peroxidation of styrene 1a to form [1,2-bis((tert-butylperoxy)ethyl)]benzene 2a by varying the reagent ratio and the nature of the catalyst. The best results were achieved with Mn(OAc)₃ (Table 1).

Table 1 Synthesis of [1,2-bis((tert-butylperoxy)ethyl)]benzene 2a from styrene 1a and tert-butyl hydroperoxide using compounds of manganese as catalyst

<table>
<thead>
<tr>
<th>Run</th>
<th>Molar ratio</th>
<th>Reaction time, h</th>
<th>Yield of 2a, %</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1 : 4 : 3</td>
<td>48 (CH₃CN)</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>1 : 4 : 0.2</td>
<td>48 (CH₃CN)</td>
<td>60</td>
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<tr>
<td>3</td>
<td>1 : 3 : 2</td>
<td>48 (CH₃CN)</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>1 : 3 : 0.5</td>
<td>48 (CH₃CN)</td>
<td>58</td>
</tr>
<tr>
<td>5</td>
<td>1 : 3 : 0.4</td>
<td>48 (CH₃CN)</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>1 : 3 : 0.2</td>
<td>48 (CH₃CN)</td>
<td>73</td>
</tr>
<tr>
<td>7</td>
<td>1 : 3 : 0.2</td>
<td>1 (CH₃CN)</td>
<td>46</td>
</tr>
<tr>
<td>8</td>
<td>1 : 3 : 0.1</td>
<td>48 (CH₃CN)</td>
<td>7</td>
</tr>
<tr>
<td>9</td>
<td>1 : 3 : 0.1</td>
<td>48 (CH₃CN)</td>
<td>75</td>
</tr>
<tr>
<td>10</td>
<td>1 : 3 : 0.05</td>
<td>48 (CH₃CN)</td>
<td>53</td>
</tr>
<tr>
<td>11</td>
<td>1 : 2 : 0.1</td>
<td>48 (CH₃CN)</td>
<td>60</td>
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<tr>
<td>12</td>
<td>1 : 3 : 0.1</td>
<td>48 (CH₃Cl)</td>
<td>16</td>
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<tr>
<td>13</td>
<td>1 : 3 : 0.1</td>
<td>48 (Benzene)</td>
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<td>14</td>
<td>1 : 3 : 0.1</td>
<td>48 (AcOH)</td>
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<td>1 : 3 : 0.1</td>
<td>48 (Acetone)</td>
<td>57</td>
</tr>
<tr>
<td>16</td>
<td>1 : 3 : 0.1 MnO₂</td>
<td>48 (CH₃CN)</td>
<td>43</td>
</tr>
<tr>
<td>17</td>
<td>1 : 3 : 0.3 MnO₂</td>
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<td>57</td>
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<td>18</td>
<td>1 : 3 : 0.4 MnO₃</td>
<td>48 (CH₃CN)</td>
<td>10</td>
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<tr>
<td>19</td>
<td>1 : 3 : 0.1 Mn(OAc)₃</td>
<td>48 (CH₃CN)</td>
<td>19</td>
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<tr>
<td>21</td>
<td>1 : 3 : 0.4 MnCl₂</td>
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<td>8</td>
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</table>

The introduction of a substituent in the aromatic ring or in the vinyl group (at the α-position) of styrene 1a has only a slight effect on the formation of bisperoxides. Under the conditions of run 9, bisperoxides 2b-i were prepared from styrenes 1b-i in moderate or good yields, which are, however, somewhat lower compared to 2a (Table 2). These results suggest that other structurally similar styrenes can also be used in the synthesis of the corresponding bisperoxides.

Proposed mechanism of the synthesis of bisperoxides

Based on the results of peroxidation using compounds of manganese in different oxidation states and the literature data on oxidation reactions involving manganese salts, we proposed the mechanism of the peroxidation (Scheme 2).

In the first step, the reaction of t-BuOOH with Mn(OAc)₃ can proceed via two pathways (a and b). In the reaction via the pathway a, Mn(OAc)₃ directly oxidizes t-BuOOH to form the peroxy radical t-BuOO• in the reaction via the pathway b, the acetic acid moiety is replaced with tert-butyl hydroperoxide to form Mn(V)OOH(t-Bu)CO•, which fragments on two particles (arrows c and e). The radical t-BuOO• rapidly abstracts hydrogen (step d) from t-BuOOH to give t-BuOO•- and Mn(V)OOH(t-Bu)CO•. In the pathway f, Mn(V)OOH(t-Bu)CO• is produced from Mn(V)OOH(t-Bu)CO• and t-BuOO•-.
Bu followed by the reaction of this intermediate with t-BuOOH (similarly to Mn(OAc)₃) to form O=Mn⁴⁺(OAc)OO⁻⁻t-Bu.

Based on the results of the experiment with MnO₂ (runs 16 and 17, Table 1), in which 2a was obtained in good yield, it can be supposed that O=Mn⁴⁺(OAc)OO⁻⁻t-Bu initiates a new peroxidation cycle. The radicals t-BuOO• react with styrene 1a (step g) to give the stabilized benzyl radical, which either recombines with t-BuOO• or is oxidized with Mn³⁺(OAc)₂OO⁻⁻t-Bu accompanied by the transfer of the ligand OO⁻⁻t-Bu (step h) to give the target bisperoxide 2a. Indirectly existence of benzyl radical is confirmed by the isolation of phenyloxirane which is the product of intramolecular radical substitution of t-BuO•. The compound Mn(OAc)₂ that is formed in the steps a and i is oxidized with t-BuOOH (step j) to form Mn(OAc)₃. This is how the step-by-step transformation of manganese derivatives in various oxidation states occurs in the catalytic cycle of peroxidation of the C=C bond.

**Scheme 2** Proposed mechanism of the peroxidation of styrene 1a with tert-butyl hydroperoxide using compounds of manganese

**Conclusions**

It was shown that manganese salts in oxidation states 2, 3, 4, and 7 catalyze the peroxidation of styrenes with tert-butyl hydroperoxide. A method was proposed for the synthesis of 1,2-bis(tert-butylperoxy)ethyl]arenes from readily available and cheap starting reagents. Despite a large number of elementary steps in this reaction, the peroxidation is accomplished in moderate or good yields (up to 75%). The synthesized compounds and the method for their preparation may be applied for the production of radical polymerization initiators of unsaturated monomers.

**Experimental**

Caution: Although we have encountered no difficulties in working with peroxides, precautions, such as the use of shields, fume hoods, and the avoidance of heating and shaking, should be taken whenever possible.

NMR spectra were recorded on a commercial instrument (300.13 MHz for ¹H, 75.48 MHz for ¹³C) in CDCl₃. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI). The measurements were performed in positive ion mode (interface capillary voltage 4500 V); the mass ratio was from m/z 50 to 3000 Da; external/internal calibration was done with Electrospray Calibrant Solution. A syringe injection was used for solutions in MeCN (flow rate 3 µL/min). Nitrogen was applied as a dry gas; the interface temperature was set at 180 °C.

The TLC analysis was carried out on standard silica gel chromatography plates. Chromatography was performed on silica gel (0.060-0.200 mm, 60 A, CAS 7631-86-9).

Hexane, CH₃CN, benzene, acetone, AcOH, CH₂Cl₂, ethyl acetate (EA), Mn(OAc)₃•2H₂O, Mn(OAc)₃•4H₂O, MnCl₂•4H₂O, MnO₂, and KMnO₄ were purchased from Acros.

**Experiments for Table 1 (runs 1-11).**

In a 15 ml round bottom flask, styrene 1a (0.5 g, 4.85 mmol) was dissolved in CH₃CN (10 mL). Then a 70% aqueous t-BuOOH
Experiments for Table 1 (runs 12, 13).

In a 15 ml round bottom flask, styrene 1a (0.5 g, 4.85 mmol) was dissolved in CHCl₃ or benzene (10 mL). Then a 70% aqueous t-BuOOH solution (1.87 g, 14.55 mmol, 3 mol per mole of 1a) and Mn(OAc)₂•2H₂O (0.13 g, 0.485 mmol; 0.1 mol per mole of 1a) were successively added with stirring. The heterogeneous reaction mixture was stirred at 20-25°C for 48 h. Then the reaction mixture was filtered off from manganese salts. The organic phase was washed with a saturated aqueous NaHCO₃ solution (10 mL). Then a solution of NaOAc (10 mL). Then a 70% aqueous t-BuOOH solution (1.87 g, 14.55 mmol; 3 mol per mole of 1a) and Mn(OAc)₂•2H₂O (0.13 g, 0.485 mmol; 0.1 mol per mole of 1a) were successively added with stirring. The heterogeneous reaction mixture was stirred at 20-25°C for 48 h.

Experiments for Table 2. Synthesis of bisperoxides 2b-i.

In a 15 ml round bottom flask, compound 1b-li (0.573-0.87 g, 4.85 mmol) was dissolved in CH₂CN (10 mL). Then a 70% aqueous t-BuOOH solution (1.87 g, 14.55 mmol; 3 mol per mole of 1b-li) and Mn(OAc)₂•2H₂O (0.13 g, 0.485 mmol; 0.1 mol per mole of 1b-li) were successively added with stirring. The heterogeneous reaction mixture was stirred at 20-25°C for 48 h.

1-[2,2-Bis(tert-butylperoxy)ethyl]benzene 2a

Colourless oil; Rf = 0.77 (ethyl acetate/hexane = 5:95); ¹H NMR (300.13 MHz, CDCl₃): δ 1.26 (s, 9H, t-BuOO), 1.27 (s, 9H, t-BuOO), 4.09 (dd, J = 11.5, 4.0 Hz, 1H, CH₂), 4.25 (dd, J = 11.5, 7.6 Hz, 1H, CH₂), 5.23 (dd, J = 7.6, 4.0 Hz, 1H, CH), 7.25-7.43 (m, 5H, ArH); ¹³C NMR (75.48 MHz, CDCl₃): δ 26.3, 26.4, 76.8, 80.4, 80.5, 83.3, 127.0, 127.9, 128.2, 136.8; Anal. calcd. for C₁₃H₁₄O₂: C 86.08, H 9.28; found: C 86.10, H 9.22; HRMS (ESI) calcd. for C₁₃H₁₄NO₄ [M+N⁺]: 305.1723, found: 305.1720.

1-[2,2-Bis(tert-butylperoxy)-1-methyl]ethylbenzene, 2b

Colourless oil; Rf = 0.82 (ethyl acetate/hexane = 5:95); ¹H NMR (300.13 MHz, CDCl₃): δ 1.21 (s, 9H, t-BuOO), 1.26 (s, 9H, t-BuOO), 1.67 (s, 3H, CH₃), 4.25 (m, 2H, CH₂O), 7.24-7.55 (m, 5H, ArH); ¹³C NMR (75.48 MHz, CDCl₃): δ 21.9, 26.3, 26.6, 79.2, 79.4, 80.5, 82.9, 126.1, 127.1, 127.8, 143.0; Anal. calcd. for C₁₃H₁₄O₂: C 86.98, H 9.52; found: C 86.92, H 9.74; HRMS (ESI) calcd. for C₁₃H₁₄NO₄ [M+N⁺]: 319.1880, found: 319.1876.

1-[2,2-Bis(tert-butylperoxy)ethyl]-4-methylbenzene, 2c

Colourless oil; Rf = 0.75 (ethyl acetate/hexane = 5:95); ¹H NMR (300.13 MHz, CDCl₃): δ 1.25 (s, 9H, t-BuOO), 1.26 (s, 9H, t-BuOO), 2.36 (s, 3H, CH₃), 4.08 (dd, J = 11.4, 4.0 Hz, 1H, CH₂), 4.25 (dd, J = 11.4, 7.7 Hz, 1H, CH₂), 5.19 (dd, J = 7.7, 4.0 Hz, 1H, CH), 7.17 (d, J = 8.1 Hz, ArH), 7.27 (d, J = 8.1 Hz, ArH); ¹³C NMR (75.48 MHz, CDCl₃): δ 21.2, 26.3, 26.4, 76.8, 80.4, 80.6, 83.2, 128.0, 128.9, 135.5, 137.6; Anal. calcd. for C₁₃H₁₄O₂: C 86.89, H 9.52; found: C 86.94, H 9.60; HRMS (ESI) calcd. for C₁₃H₁₄NO₂ [M+N⁺]: 314.2326, found: 314.2324.

1-[2,2-Bis(tert-butylperoxy)ethyl]-4-tert-benzylbenzene, 2d

Colourless oil; Rf = 0.8 (ethyl acetate/hexane = 5:95); ¹H NMR (300.13 MHz, CDCl₃): δ 1.25 (s, 9H, t-BuOO), 1.27 (s, 9H, t-BuOO), 1.32 (s, 9H, t-BuOO), 2.36 (s, 3H, CH₃), 4.09 (dd, J = 11.4, 4.0 Hz, 1H, CH₂), 4.25 (dd, J = 11.4, 7.7 Hz, 1H, CH₂), 5.20 (dd, J = 7.7, 4.0 Hz, 1H, CH), 7.30 (d, J = 8.1 Hz, ArH), 7.37 (d, J = 8.1 Hz, ArH); ¹³C NMR (75.48 MHz, CDCl₃): δ 26.3, 26.4, 31.3, 34.5, 76.9, 80.4, 80.6, 83.2, 125.2, 126.7, 135.5, 150.7; Anal. calcd. for C₁₅H₁₄O₂: C 70.97, H 10.12; found: C 70.99, H 10.15; HRMS (ESI) calcd.
for C_{20}H_{33}NaO_4 [M+Na^+]: 361.2349, found: 361.2335.

1-[1,2-Bis(2-propenylperoxy)ethyl]-4-methoxybenzene, 2e
Colourless oil; R_t = 0.51 (ethyl acetate/hexane = 5:95); 1^1 H NMR (300.13 MHz, CDCl_3): δ 1.24 (s, 9H, t-BuOO), 1.25 (s, 9H, t-BuOO), 3.81 (s, 3H, CH_3O), 4.08 (dd, J = 11.4, 4.3 Hz, 1H, CH_2), 4.26 (dd, J = 11.4, 7.4 Hz, 1H, CH_2), 5.15 (dd, J = 7.5, 4.3 Hz, 1H, CH), 6.89 (d, J = 8.6 Hz, 2H, ArH), 7.29 (d, J = 8.6 Hz, 2H, ArH); 13^1 C NMR (75.48 MHz, CDCl_3): δ 26.3, 26.4, 55.2, 76.7, 80.4, 80.5, 82.8, 113.7, 128.4, 130.7, 159.4; Anal. calcd. for C_{13}H_{20}O_3: C 65.36, H 9.03; found: C 65.41, H 9.07; HRMS (ESI) calcd. for C_{13}H_{20}NO_3 [M+NH_4^+]: 330.2275, found: 330.2275.

1-[1,2-Bis(2-propenylperoxy)ethyl]-2-methoxybenzene, 2f
Colourless oil; R_t = 0.55 (ethyl acetate/hexane = 5:95); 1^1 H NMR (300.13 MHz, CDCl_3): δ 1.26 (s, 9H, t-BuOO), 1.28 (s, 9H, t-BuOO), 3.83 (s, 3H, OCH_3), 4.08 (dd, J = 11.1, 7.9 Hz, 1H, CH), 4.17 (dd, J = 11.1, 3.1 Hz, 1H, CH), 5.60 (dd, J = 11.1, 7.9 Hz, 1H, CH), 6.84-6.89 (m, 1H, ArH), 6.94-7.01 (m, 1H, ArH), 7.23-7.29 (m, 1H, ArH), 7.44-7.48 (m, 1H, ArH); 1^1 C NMR (75.48 MHz, CDCl_3): δ 26.3, 26.4, 55.3, 76.0, 78.8, 80.4, 80.6, 110.4, 120.4, 126.7, 127.8, 128.7, 156.7; Anal. calcd. for C_{12}H_{18}O_4: C 64.36, H 9.03; found: C 64.31, H 9.11; HRMS (ESI) calcd. for C_{12}H_{18}NO_4 [M+Na^+]: 330.2275, found: 330.2275.

[1,2-Bis(3-propenylperoxy)ethyl]-1-phenylethylbenzene, 2g
Colourless oil; R_t = 0.71 (ethyl acetate/hexane = 5:95); 1^1 H NMR (300.13 MHz, CDCl_3): δ 1.11 (s, 9H, t-BuOO), 1.23 (s, 9H, t-BuOO), 4.83 (s, 2H, CH_2), 7.23-7.35 (m, 10H, ArH); 13^1 C NMR (75.48 MHz, CDCl_3): δ 26.3, 26.6, 77.6, 79.6, 80.5, 85.7, 127.3, 127.5, 127.8, 142.1; Anal. calcd. for C_{20}H_{24}O_4: C 73.71, H 8.44; found: C 73.69, H 8.50; HRMS (ESI) calcd. for C_{20}H_{24}NO_4 [M+Na^+]: 381.2036, found: 381.2031.

1-[1,2-Bis(2-propenylperoxy)ethyl]naphthalene, 2h
Colourless oil; R_t = 0.77 (ethyl acetate/hexane = 5:95); 1^1 H NMR (300.13 MHz, CDCl_3): δ 1.31 (s, 9H, t-BuOO), 1.34 (s, 9H, t-BuOO), 4.22-4.33 (m, 2H, CH_2), 6.08-6.15 (m, 15H, CH), 7.46-7.59 (m, 3H, ArH), 7.69-7.76 (m, 1H, ArH), 7.78-7.93 (m, 2H, CH), 8.18-8.24 (m, 1H, ArH); 13^1 C NMR (75.48 MHz, CDCl_3): δ 26.3, 26.5, 77.0, 80.5, 80.7, 80.8, 123.2, 124.4, 125.4, 126.0, 128.2, 128.8, 130.9, 133.8, 134.2; Anal. calcd. for C_{20}H_{24}O_4: C 72.26, H 8.49; found: C 72.38, H 8.30; HRMS (ESI) calcd. for C_{20}H_{24}NO_4 [M+Na^+]: 355.1880, found: 355.1869.

1-[1,2-Bis(2-propenylperoxy)ethyl]-4-chlorobenzene, 2i
Colourless oil; R_t = 0.69 (ethyl acetate/hexane = 5:95); 1^1 H NMR (300.13 MHz, CDCl_3): δ 1.23 (s, 9H, t-BuOO), 1.24 (s, 9H, t-BuOO), 4.03 (dd, J = 11.7, 4.2 Hz, 1H, CH_2), 4.19 (dd, J = 11.7, 7.5 Hz, 1H, CH_2), 5.19 (dd, J = 7.5, 4.2 Hz, 1H, CH), 7.26-7.35 (m, ArH); 13^1 C NMR (75.48 MHz, CDCl_3): δ 26.2, 26.3, 76.4, 80.5, 80.7, 82.6, 128.4, 128.5, 133.6, 137.2; Anal. calcd. for C_{15}H_{12}ClO_4: C 60.66, H 7.95, Cl 11.19, found: C 60.44, H 7.62, Cl 11.20; HRMS (ESI) calcd. for C_{15}H_{12}ClO_4 [M+Na^+] : 334.1780, found: 334.1774.

2-Phenoxyxirane
Colourless oil; R_t = 0.39 (ethyl acetate/hexane = 5:95); 1^1 H NMR (300.13 MHz, CDCl_3): δ 2.82 (dd, J = 5.50, 2.57 Hz, 1H, CH_3), 3.16 (dd, J = 5.50, 4.04 Hz, 1H, CH_3), 3.88 (dd, J = 4.04, 2.57 Hz, 1H, CH), 7.23-7.45 (m, ArH); 13^1 C NMR (75.48 MHz, CDCl_3): δ 51.1, 52.2, 125.4, 128.1, 128.4, 137.6.

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Notes and references
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