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Selective copper(II)-catalyzed aerobic oxidative cleavage of aromatic *gem*-disubstituted alkenes to carbonyl compounds under neutral and mild conditions

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ABSTRACT

Three copper(II) catalytic systems, $CuCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$+phenanthroline, and $[Cu(\mu\text{-}Cl)Cl(phen)]_2$ were used to cleave alkenes to their corresponding carbonyl compounds under aerobic and neutral conditions. $[Cu(\mu\text{-}Cl)Cl(phen)]_2$ shows enhanced selectivity over the other two catalytic systems. The oxidative cleavage reactions were carried out in mixed H_2O/THF solvent system under oxygen (4 atm) at 60°C. The real oxidant is 2-hydroperoxytetrahydrofuran, which is generated *in situ* in the process through the reaction between THF and oxygen catalyzed by copper(II). The cleavage reactions are selective for aromatic *gem*-disubstituted alkenes. Aromatic internal alkenes are slow to be oxidized, and both aliphatic terminal and internal alkenes are inert to oxidative cleavage. Free radical scavenger 2,2,6,6, tetramethylpiperidinyl-1-oxyl (TEMPO) deactivates the reaction indicating the involvement of free radical path in the reaction mechanism.

1. Introduction

Alkene oxidation reactions are of diverse utility with immense impact on the development of synthetic organic chemistry.[1] In particular, oxidative cleavage of olefins to the corresponding carbonyl compounds is pivotal for the preparation of valuable intermediates and fine chemicals.[2] There are numerous diverse methods to accomplish this oxidation. Among those, ozonolysis is a classical one, which involves in direct oxidative cleavage of the C=C double bond in alkenes.[3] However, its utility is often limited due to safety concerns.[4] Transition metals, such as Ru,[5] Os,[6] Mn,[7] W,[8] Re,[9] Pd,[10] Fe,[11] and Au[12] were used to catalyze the cleavage reaction without using ozone, and transition metal free aryl-λ^3-iodane-based methods have also been reported.[13] In spite of great progress in the field of oxidative cleavage of alkenes, processes that involve inexpensive and green catalysts are scarce.

Regarding oxidant, for simplicity and easy availability, molecular oxygen is one of the ultimate goals in oxidation chemistry. However, transition metal catalyzed C=C double bond cleavage reactions by oxygen are quiet limited, and in most cases reactions are not selective.[14] Thus, the development of a safe, simple, and green protocols for selective alkene aerobic oxidation is highly desirable.

The use of copper salts and complexes as the catalysts has gained much prominence recently because of their economic viability, less hazardous, good functional group tolerance, and scalability in large-scale synthetic procedures. Copper is involved in the cleavage of different types of C–C single bonds,[15] C=C double bonds in ketenimines[16] and aromatic enol ethers,[17] C≡C triple bonds in *O*-propargyl oximes,[18] and aromatic ring cleavage in catechol.[19] Copper containing enzyme laccase is also used to cleave the alkene double bond.[20] Use of $CuCl_2$ in the electrochemical oxidation of styrene in the presence of oxygen is also reported.[21] Although biological[20] and electrochemical[21] cleavage of the C=C double bond involving copper have been reported, aerobic oxidative cleavage of alkene to carbonyl compounds using copper salts or complexes is rare.[22] Herein, we report selective Cu(II) catalyzed aerobic oxidative cleavage of the C=C double bonds of *gem*-disubstituted alkenes to the corresponding ketones. Possible reaction paths are also proposed.

2. Results and discussion

Alkene 1,1-diphenylethylene was used as the starting substrate. The oxidation reaction is excellent in yield using the recently reported oxidation catalyst $[Cu(\mu\text{-}Cl)Cl(phen)]_2$ (**1**).[23] However, the control reaction, i.e., oxidation using $CuCl_2 \cdot 2H_2O$ alone, produced similar results under similar conditions. The reaction conditions were then optimized in different solvents with different catalytic

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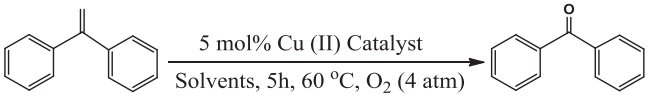
systems: $CuCl_2 \cdot 2H_2O$ (**A**), $CuCl_2 \cdot 2H_2O$+phenanthroline (**B**), and complex **1** (**C**). The results are summarized in Table 1.

Table 1
Optimization of the reaction conditions for aerobic oxidation of 1,1-diphenylethylene in different solvents and Cu(II) catalytic systems



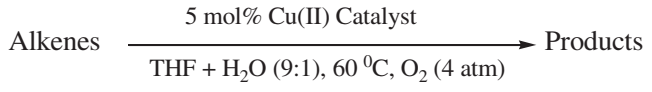
Entry	Solvents	O_2	Catalyst used	Yield %[a]		
				A[b]	**B**[c]	**C**[d]
1	Toluene	Yes	Yes	—[e]	—	—
2	*n*-Pentane	Yes	Yes	—	—	—
3	CH_3CN	Yes	Yes	—	—	—
4	CH_2Cl_2	Yes	Yes	—	—	—
5	THF	Yes	Yes	Trace	Trace	Trace
6	THF+H_2O (9:1)	Yes	Yes	91	89	98
7	THF+H_2O (9:1)	Yes[f]	Yes	—	—	53[g]
8	THF+H_2O (9:1)	No	Yes	—	—	—
9	THF+H_2O (9:1)	Yes	No	—	—	—
10	THF+H_2O (1:1)	Yes	Yes	—	—	—
11	H_2O	Yes	Yes	—	—	—

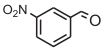
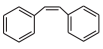
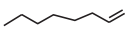
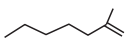
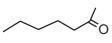
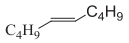
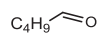
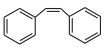
[a] Yields were determined by GC based on 100% conversion.
[b] $CuCl_2 \cdot 2H_2O$.
[c] $CuCl_2 \cdot 2H_2O$+phenanthroline.
[d] $[Cu(\mu\text{-}Cl)Cl(phen)]_2$.
[e] No reaction.
[f] 2 atm.
[g] 67% conversion.

Oxidation reactions for all the three catalytic systems (**A**, **B**, and **C**) were carried out in polar (CH_3CN, CH_2Cl_2, THF, and H_2O), non-polar (toluene and *n*-pentane), and mixed solvent systems (THF+H_2O) (Table 1). Reactions in polar and nonpolar solvents were unsuccessful (entries 1–5 and 11). Using mixed solvent of THF and water with THF to water ratio 9:1 (v/v) achieved good yield (entry 6). However, water and THF alone were found to be unsuitable (entries 5 and 11). It is also clear that both oxygen and Cu(II) are needed (entries 8 and 9). All the three catalytic systems can cleave the alkene to form the corresponding ketone (entry 6). Under 2 atm of oxygen, lower yield (53%) was obtained (entry 7). Instead of phenanthroline, bulky ligands, such as neocuproine and bathocuproine afforded similar yields (83% and 85% with 100% conversion, respectively) and selectivity under identical reaction conditions.

Catalytic systems (**A**, **B**, and **C**) were applied to various alkenes in THF/H_2O and the results are summarized in Table 2. Aromatic *gem*-disubstituted alkenes were successfully oxidized to their corresponding ketones with high yields and selectivity (entries 4–7). Among these Cu(II) catalytic systems, **C** afforded the highest selectivity. The aromatic mono-substituted alkenes are less selective (entries 1–3) irrespective of electronically neutral (entry 1), rich (entry 2), or poor (entry 3) alkenes. Aliphatic mono-substituted (entry 9), *gem*-disubstituted (entry 10), and internal alkene (entry 11) are inert. Furthermore, the internal aromatic alkene is much less reactive than the terminal aromatic alkenes (entry 8). The selectivity is demonstrated by the reaction of equimolar amounts of mixed terminal and internal alkenes, which leads to the products with much higher yield in the terminal alkene (entry 12), and **C** is more effective for the selectivity among the three catalytic systems. Although regioselective oxidation of alkenes to epoxides is well known,[24] examples of the cleavage of alkene double bonds are rare.[25] The observed selectivity in Table 2 may be useful in synthetic organic chemistry when there are different types of double bonds in the same substrate. At the end of the oxidation reaction, the Cu(II) catalyst was still active because further conversion of the

Table 2
Aerobic oxidation of alkenes into aldehydes and ketones



Entry	Alkenes	Products	Yield %[a,b]		
			A[c]	**B**[d]	**C**[e]
1			31/19 (10)[f]	29 (5)	Trace (15)
2			28/17 (10)	24 (15)	Trace (15)
3			21/16 (20)	11 (20)	18 (30)
4			91 (5)	89 (5)	98/93 (5)
5			85 (5)	85 (7)	98/91 (15)
6			81 (7)	83 (7)	96/89 (15)
7			80 (7)	83 (7)	97/90 (15)
8			15[g] (10)	11[h]	(10) 5[i] (15)
9			—[j] (10)	— (10)	— (15)
10			— (10)	— (10)	— (15)
11			— (10)	— (10)	— (15)
12			11[k] (5)	10[l] (5)	4[m] (5)
			61 (5)	63 (5)	73 (5)

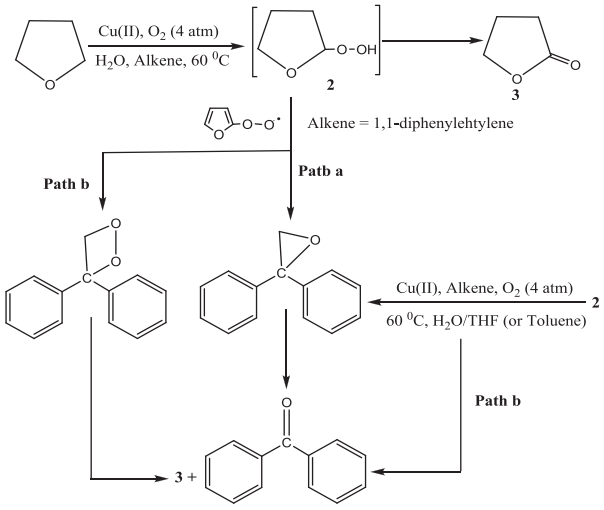
[a] Yields were determined by GC based on 100% conversion except internal alkene in the entries 8 and 12.
[b] Isolated yields.
[c] $CuCl_2 \cdot 2H_2O$.
[d] $CuCl_2 \cdot 2H_2O$+phenanthroline.
[e] $[Cu(\mu\text{-}Cl)Cl(phen)]_2$.
[f] Figures in parenthesis are reaction time in hours.
[g] Conversion 23%.
[h] Conversion 19%.
[i] Conversion 12%.
[j] No reaction.
[k] Conversion 19%.
[l] Conversion 17%.
[m] Conversion 8%.

alkene to the corresponding ketone was observed when additional alkene (e.g., 1,1-diphenylethylene) was added to the reaction mixture.

Oxidation of alkenes to carbonyl compounds exclusively in the THF solvent (although it is trace in pure THF, Table 1, entry 5) indicates a vital role of the solvent in the process. In this study, the ideal solvent system is the mixed solvent of THF and water (9:1 v/v ratio; Table 1, entry 6), however, excess water is not effective (Table 1, entry 10). These observations indicate that only a small portion of water in the mixed solvent is required for the oxidation and excess of water inhibits the process.

Furthermore, THF or water alone is also unsuitable (Table 1, entries 5 and 11). It has been reported that Rh catalyzed formation

of 2-hydroperoxytetrahydrofuran (**2**) from THF requires small amount of water, and larger amount of water inhibits the reaction.[26] Detection of γ-butyrolactone (**3**), the decomposition product of **2**, in the reaction further supports the formation of **2** during catalytic reactions (Figs. S15–S29 in Supplementary data).[27] In addition, blank reactions reveal that the formation of **2** requires the presence of both catalyst (Cu(II)) and alkene since absence of either of them makes the cleavage reaction or formation of **3** ineffective. Therefore, the role of copper is to catalyze the formation of **2** from THF in the presence of alkene, O_2, and H_2O and may also take part in the decomposition of **2** to **3** (Scheme 1). Based on these observations, **2** is proposed to be the real oxidant in the alkene cleavage reactions because besides of THF, all the other solvents (CH_2Cl_2, CH_3CN, toluene, pentane and water) are unable to carry out the reaction under identical conditions (Table 1, entries 1–4, 11).

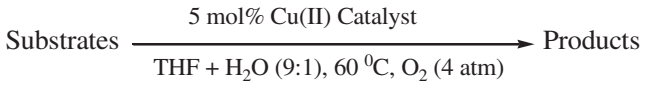


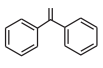
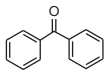
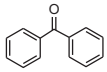
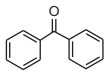
Scheme 1. Proposed reaction paths for the alkene oxidative cleavage.

Oxidative cleavage of alkenes by hydroperoxides is generally proceeded through free radical pathways.[28] For metal ion catalyzed hydroperoxy reactions, the most important function of the catalyst is the decomposition of relatively stable hydroperoxides into radical.[28] The cleavage reactions of alkenes in our case were completely inhibited in the presence of radical scavenger TEMPO (Table 3, entries 1 and 2), which is in support of the free radical pathways. However, it is still not clear whether it is a direct peroxide free radical oxidation or copper-catalyzed oxidation of alkenes by peroxide **2**.

To clarify the above, **2** was prepared,[29] and alkene oxidations using **2** with and without Cu(II) were carried out under identical conditions (Table 4). Cleavage reaction was incomplete (Table 4, entry 1) in the absence of **A**, however, the reaction was completed when **A** was used as a catalyst (Table 4 entry 2). This indicates the involvement of Cu(II) as a catalyst in the cleavage reactions. The reactions with **2** were also carried out in toluene to verify the influence of extra **2** possibly formed *in situ* during the catalytic process in THF/H_2O solvent system. The results of the cleavage reactions with and without catalyst **A** under identical conditions in toluene are comparable to those in THF (Table 4, entry 3 and 4) indicating the extra **2** formed *in situ* is minor as compared to the pure **2** added. The reaction between alkene and **2** under inert atmosphere (1 atm nitrogen) producing the corresponding carbonyl compound further supports the argument (Table 4, entries 5 and 6).

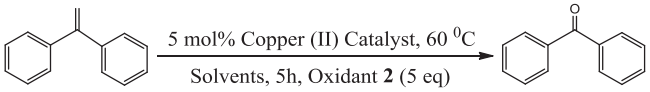
Table 3
Control reactions of alkenes and epoxides



Entry	Alkene & epoxide	Products	Catalyst	TEMPO[b]	GC yield[a] %		
					A[c]	**B**[d]	**C**[e]
1[g]			Yes	Yes	—[f]	—	—
2[g]			Yes	Yes	—	—	—
3[g]			Yes	No	24	14	17
4[g]			No	No	—	—	—
5[h]			Yes	No	53	41	49
6[h]			No	No	—	—	—

[a] Yields were determined by GC based on 100% conversion.
[b] TEMPO (46.8 mg, 0.3 mmol).
[c] $CuCl_2 \cdot 2H_2O$.
[d] $CuCl_2 \cdot 2H_2O$+phenanthroline.
[e] $[Cu(\mu\text{-}Cl)Cl(phen)]_2$.
[f] No reaction.
[g] Reaction time 15 h.
[h] Reaction time 5 h.

Table 4
Control reactions for aerobic oxidation of 1,1-diphenylethylene in different solvents and oxidant **2**



Entry	Solvents (9:1)	**A**[a]	Conv./yield%[b]
1[c]	THF/H_2O	No	45/34
2[c]	THF/H_2O	Yes	100/81
3[c]	Toluene+H_2O	No	47/37
4[c]	Toluene+H_2O	Yes	100/83
5[d]	THF/H_2O	Yes	65/17
6[d]	Toluene+H_2O	Yes	71/21

[a] $CuCl_2 \cdot 2H_2O$.
[b] Yields were determined by GC (Figs. S26–S29 in Supplementary data).
[c] Reaction under O_2 (4 atm).
[d] Reaction under 1 atm nitrogen.

The alkene cleavage may go through the epoxide as an intermediate, and alkylperoxy radical may involve in the alkene oxidation to epoxide. It might proceed in two steps: initially via epoxidation of alkene and its subsequent oxidation to the carbonyl compound (path **a** in Scheme 1).[30] In addition, trace amount of epoxides (styrene oxide and 1,1-diphenylethylene oxide) were observed in the final reaction mixture of the corresponding reactions (Figs. S15–S17 and S26–S28 in Supplementary data).

The oxidation of styrene epoxide and 1,1-diphenylethylene oxide afforded the respective carbonyl compounds (Table 3, entries 3 and 5) indicating that epoxides could be the intermediates formed in the reactions. The reactions in the absence of Cu(II) were unsuccessful (Table 3, entries 4 and 6) indicating Cu(II) is essential in the carbon elimination of epoxide to form the carbonyl compound.

Alkene cleavage via dioxetane without going through epoxide however cannot be totally eliminated (path b in Scheme 1).[31]

3. Conclusion

In conclusion, the Cu(II) catalyst systems (**A**, **B**, and **C**) can selectively catalyze the aerobic oxidative cleavage of terminal C=C double bonds in aromatic *gem*-disubstituted alkene with high yield at low temperature. The catalytic systems involve the coupling of two oxidation reactions, i.e., the oxidation of THF to **2** and the oxidative cleavage of alkene, in one-pot.

4. Experimental section

4.1. General

All chemicals were obtained from commercial sources and used without further purification. Phenanthroline, neocuproine, 2,2,6,6, tetramethylpiperidinyl-1-oxyl (TEMPO), α-methylstyrene, styrene, styrene oxide, 4-chloro-α-methylstyrene, *cis*-stilbene, 1,1-diphenyl ethylene, 3-nitrostyrene, 3-nitrobenzaldehyde, 1,1-diphenyethy lene oxide, valeraldehyde, benzaldehyde, 4-chloroacetophenone, acetophenone, 4-fluoroacetophenone, heptaldehyde, 1-octene, γ-butyrolactone, 2,3-dihydrofuran, ammonium chloride, and cupric chloride dihydrate were purchased from Across. *trans*-5-Decene, 3-methylstyrene, 4-fluoro-α-methylstyrene, benzophenone, and *m*-tolualdehyde were purchased from Alfa Aesar. Bathocuproine, 2-methyl-1-1-heptene and 34.5–36.5 wt. % aqueous solution of H_2O_2 were purchased from Aldrich. $[(phen)Cu(\mu\text{-}Cl)(Cl)]_2$ and 2-hydroperoxytetrahydrofuran were synthesized according to literature.[23,29] Gas chromatographic analyses were performed on an Agilent 6890 instrument with an FID detector and an Agilent 30 m×0.53 mm×3.0 μm HP-1 capillary column. Products isolation was carried out by TLC (Merck, TLC silica gel 60 F_{254} 25 Aluminum sheets 20×20 cm). NMR spectra were recorded in $CDCl_3$ on a Bruker AV 400 MHz.

4.2. Typical procedure for alkene oxidation

A stock solution of $CuCl_2 \cdot 2H_2O$ in water (0.0171 g/cc) was prepared. To a Pyrex tube with a Teflon screw cap and side arm inlet, catalyst **A** (100 μL of the stock solution, 0.01 mmol of $CuCl_2$), or **B** (100 μL of a stock solution, 0.01 mmol of $CuCl_2$, 2.0 mg, 0.01 mmol of phenanthroline), or **C** (6.3 mg, 0.01 mmol+100 μL water) was added. Then 900 μL of THF and 0.2 mmol of alkene were added in each case. The tube was filled with oxygen (4 atm) and heated to 60 °C with stirring till to its reaction time specified in Table 2. The reaction mixture was cooled and diluted with ethyl acetate. Internal standard 1,4-di-*tert*-butylbenzene (11.9 mg, 0.06 mmol) was then added, and the products were analyzed by GC. Similar procedure was followed for each alkene and reactions of alkene and epoxide with TEMPO (46.8 mg, 0.3 mmol).

4.3. Typical oxidation of 1,1-diphenylethylene by 2-hydrope roxytetrahydrofuran (2)

To a Pyrex tube with a Teflon screw cap and side arm inlet, THF (900 μL), H_2O (100 μL), 1,1-diphenylethylene (0.2 mmol, 35.7 μL), and **2** (1.0 mmol, 104.0 mg) were added. The tube was filled with oxygen (4 atm) and heated to 60 °C with stirring for 5 h. The reaction mixture was cooled and diluted with ethyl acetate. Internal standard 1,4-di-*tert*-butylbenzene (11.9 mg, 0.06 mmol) was then added, and the products were analyzed by GC. Similar procedure was followed for the reaction in toluene (900 μL). For the reactions with catalyst **A** (100 μL of the stock solution, 0.01 mmol of $CuCl_2$) and 900 μL of solvent THF or toluene were used for each case under identical conditions. The products were also analyzed by GC with the same procedure stated above.

4.3.1. Benzaldehyde. TLC (hexane/ethyl acetate=1:0.5) gave benzaldehyde as a colorless liquid; yield: 4 mg (19%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.98 (s, 1H), 7.85–7.47 (m, 5H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 192.1, 136.2, 134.2, 129.5, 128.8.

4.3.2. m-Tolualdehyde. TLC (hexane/ethyl acetate=1:0.5) gave *m*-tolualdehyde as a colorless liquid; yield: 4 mg (17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.95 (s, 1H), 7.65–7.64 (m, 2H), 7.42–7.26 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 192.7, 139.1, 136.7, 135.5, 130.2, 129.1, 127.4, 21.4.

4.3.3. 3-Nitrobenzaldehyde. TLC (hexane/dichloromethane=1:1) gave 3-nitrobenzaldehyde as a colorless solid; yield: 5 mg (16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 10.11 (s, 1H), 8.67–8.66 (m, 1H), 8.46–8.44 (m, 1H), 8.23–8.21 (m, 1H), 7.76 (t, *J*=7.9 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 189.9, 148.9, 137.5, 134.9, 130.5, 128.7, 124.4.

4.3.4. Benzophenone. TLC (hexane/ethyl acetate=1:0.5) gave benzophenone as a colorless solid; yield: 34 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.80 (d, *J*=7.8 Hz, 4H), 7.57 (t, *J*=7.6 Hz, 1H), 7.47 (t, *J*=7.6, 4H), ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 196.9, 137.8, 132.6, 130.2, 128.5.

4.3.5. Acetophenone. TLC (hexane/ethyl acetate=1:0.5) gave acetophenone as a colorless liquid; yield: 22 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.87 (d, *J*=7.6 Hz, 2H), 7.50–7.46 (m, 1H), 7.40–736 (m, 2H), 2.51 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 198.1, 137.1, 133.1, 128.6, 128.3, 26.6.

4.3.6. 4-Fluoroacetophenone. TLC (hexane/ethyl acetate=1:0.5) gave 4-fluoroacetophenone as a colorless liquid; yield: 24 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.95–7.91 (m, 2H), 7.09–7.05 (m, 2H), 7.40–736 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 196.6, 167.2, 164.7, 133.8, 131.2, 131.1, 115.9, 115.7, 26.7.

4.3.7. 4-Chloroacetophenone. TLC (hexane/ethyl acetate=1:0.5) gave 4-chloroacetophenone as a colorless liquid; yield: 28 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.85–7.83 (m, 2H), 7.38–7.26 (m, 2H), 2.54 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 196.9, 139.7, 135.6, 129.9, 129.0, 26.7.

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Supplementary data

Supplementary data (^{1}H NMR, ^{13}C, and important GC spectra) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.11.075.

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