FULL PAPER

# Multiwalled Carbon Nanotubes Supported Pd(II)-Salen Complex: An Effective, Phosphorous-Free, and Reusable Heterogeneous Precatalyst for the Synthesis of Diaryl Ketones

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The *Suzuki–Miyaura* cross-coupling reaction of aroyl chlorides and arylboronic acids has been carried out efficiently in the presence of Pd(II)-salen@MWCNTs as an air-moisture stable precatalyst. The influence of various parameters, such as solvent, temperature, and base on the reaction system, was studied. Furthermore, the catalyst can be easily recovered quantitatively by a simple filtration and reused for three consecutive runs without significant loss of its activity.

**Keywords:** Palladium complex, Multiwalled carbon nanotubes, *Suzuki–Miyaura* coupling, Aromatic ketones, Aroyl chlorides, Arylboronic acids.

## Introduction

The synthesis of diaryl ketones is an active area in organic synthesis since they are ubiquitous in natural products [1a], pharmaceuticals [2], and materials science [3]. For example, fenofibric acid is an aromatic ketone, which is a lipid regulating agent and is used in treatment of high cholesterol and triglyceride levels in the blood [1b].

The traditional approach for the introduction of ketone moiety into the aromatic skeletons is the *Friedel–Crafts* acylation [4]. However, low functional group tolerance, poor regioselectivity, and formation of undesired side products have limited these reactions to be employed to their full potential [5]. The nucleophilic addition of organometallic reagents like organozinc [6], Cd [7], and Sn [8] to carboxylic acid derivatives is an alternative method that addresses the problems of drastic reaction conditions and low product yields due to the formation of tertiary alcohols. Thus, the development of a mild as well as highly efficient method for the preparation of diaryl ketones has been receiving increasing interest.

To date, Pd-mediated acylation reactions are the reaction of choice for the industrial scale formation of costly fine chemicals due to the simplicity, environmentally friendly nature, and economical aspects [9]. These efficient methodologies mainly include carbonylative *Suzuki–Miyaura* reactions [10 – 12] and direct *Suzuki–Miyaura* acylation of organoboronic acids [13]. The latter approach was discovered first by *Bumagin* and co-workers who could successfully cross-couple acyl chlorides with arylboronic acids in the presence of $PdCl_2$ in aqueous acetone [14]. Since then, several improvements on Pd-catalyzed coupling reactions of carboxylic acids [15] and their derivatives, including acid chlorides [13], anhydrides [16], thioesters [17], and 2-pyridyl esters [18] with boronic acids have been widely described. Most of the above protocols are homogeneous in nature suffering from several drawbacks, such as contamination of both metal and ligand residues in the final products, recovery of the catalyst, and destruction of the catalyst during the course of the reaction. These factors have been a major driving force for designing heterogeneous catalysts by encapsulation or immobilization of catalytically active metal complexes on solid supports such as carbon nanotubes (CNTs) [19 – 21], polymers [22], and mesoporous silica [23][24]. In spite of the significant advances in this field, only a few reports have employed heterogeneous palladium complexes as a catalyst for the acylation reaction of boronic acids. For instance, silica-supported phosphine palladium(0) complex [25], Pd/C catalytic system [26], and palladium catalyst anchored to $SiO_2$ functionalized with $\equiv Si(CH_2)_3NHCH_2SMe$ [27] have been applied to the phenylation of acyl chlorides. However, disadvantages including moderate yields and formation of homocoupling adducts have limited the scope of these strategies.

In connection with our insights about the use of heterogeneous catalysts in the organic transformations [28], we describe herein a mild, and efficient Cu- and phosphine-free approach for the preparation of diaryl ketones employing our introduced multiwalled carbon nanotubes functionalized with a Pd(II)-*Schiff* base complex (Pd(II)-salen@MWCNTs) as a precatalyst [28a].

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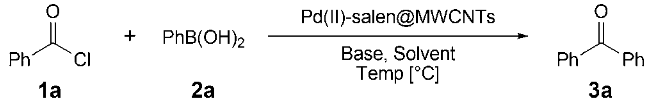
## Results and Discussion

In the first instance, the reaction conditions, such as solvent, catalyst concentration, base, and temperature, were optimized for the *Suzuki–Miyaura* cross-coupling reaction of phenylboronic acid and benzoyl chloride as the test substrates. The best molar ratio of benzoyl chloride (**1a**)/phenylboronic acid (**2a**)/$K_2CO_3$ was found to be 2:1:2.5. In order to find out the best reaction medium, the influence of various solvents was primarily investigated. While moderate yield of the coupling product (79%) was obtained when neat acetone was used as the solvent (*Entry 1*, *Table 1*), the addition of $H_2O$ increased the rate as well as the yield of the reaction (*Entries 2 – 4*, *Table 1*); among the ratios tested, the (1:1) ratio of acetone/$H_2O$ was found to be the most effective (*Entry 2*, *Table 1*). Also, the yield dropped significantly to 31% in neat $H_2O$ (*Entry 5*, *Table 1*). In addition, no satisfactory result was obtained under the solvent-free conditions and trace amount of product was formed (*Entry 6*, *Table 1*). Moderate yields of the coupling product were obtained in other solvents such as toluene and EtOH (*Entries 7 – 9*, *Table 1*). Next, the role of the catalyst concentration in the yield and the rate of the reaction was screened; using 0.9 mol-% of the catalyst led to 91% of benzophenone in 1 h (*Entry 11*, *Table 1*), whereas the yield dramatically decreased when 0.6 mol-% of the catalyst was used for the coupling reaction (*Entry 10*, *Table 1*). Moreover, using 1.05 mol-% of the heterogeneous Pd(II)-salen@MWCNTs had no marked effect on the rate of the reaction (*Entry 12*, *Table 1*). Due to the important role of the base in the Pd-catalyzed coupling reactions, the influence of various inorganic and organic bases were studied. It was observed that $K_2CO_3$ was the most effective base, while other bases including $Na_2CO_3$, $K_3PO_4$, $Cs_2CO_3$, and $Et_3N$ exhibited weaker performances (*Entries 13 – 16*, *Table 1*). However, reducing the temperature to 40 and 25 °C resulted in the formation of the target product in 82% and 57% yields, respectively (*Entries 17* and *18*, *Table 1*). To determine the scope of the substrates, further experiments with diverse acyl chlorides and arylboronic acids were carried out under the optimized reaction conditions (*Scheme 1*) and results are listed in *Table 2*. The coupling reaction of either 4-methyl- or 4-methoxybenzoyl chloride as electron-rich acyl chlorides with phenylboronic acid afforded the corresponding products in 86% and 83% yields, respectively (*Entries 2* and *3*, *Table 2*). Furthermore, aroyl chlorides bearing electron-deficient substituents, such as 4-nitro- and 4-chlorobenzoyl chloride, gave higher yields while significantly accelerated the rate of the coupling reaction (*Entries 4* and *5*, *Table 2*). Upon treatment of the sterically demanding 2-fluorobenzoyl chloride with phenylboronic acid, the desired fluorinated benzophenone was formed in 71% yield (*Entry 7*, *Table 2*). It should be pointed out that heteroaroyl chlorides, such as 2-furoyl- and 2-thenoyl chloride, were effectively cross-coupled with phenylboronic acid in short reaction times (87% and 81%, respectively; *Entries 8* and *9*, *Table 2*). Subsequently, the effect of varying substituents on arylboronic acids was also screened and no spectacular electronic effect was observed in the cross-coupling reaction (*Entries 1*, *10*, and *11*, *Table 2*).

Table 1. Optimization of the reaction conditions for the cross-coupling reaction of benzoyl chloride and phenylboronic acid[a])



| *Entry* | Solvent [ratios] | Base | Cat. [mol-%] | T [°C] | Time [h] | Yield [%][b]) |
|---|---|---|---|---|---|---|
| *1* | Acetone | $K_2CO_3$ | 0.75 | 50 | 2 | 79 |
| *2* | Acetone/$H_2O$ [1:1] | $K_2CO_3$ | 0.75 | 50 | 2 | 87 |
| *3* | Acetone/$H_2O$ [1:2] | $K_2CO_3$ | 0.75 | 50 | 2 | 83 |
| *4* | Acetone/$H_2O$ [1:3] | $K_2CO_3$ | 0.75 | 50 | 2 | 80 |
| *5* | $H_2O$ | $K_2CO_3$ | 0.75 | 50 | 2 | 31 |
| *6* | – | $K_2CO_3$ | 0.75 | 50 | 2 | Trace |
| *7* | Toluene | $K_2CO_3$ | 0.75 | 50 | 2 | 76 |
| *8* | Toluene (dry) | $K_2CO_3$ | 0.75 | 50 | 2 | 73 |
| *9* | EtOH | $K_2CO_3$ | 0.75 | 50 | 2 | 61 |
| *10* | Acetone/$H_2O$ [1:1] | $K_2CO_3$ | 0.6 | 50 | 2 | 70 |
| *11* | Acetone/$H_2O$ [1:1] | $K_2CO_3$ | 0.9 | 50 | 1 | 91 |
| *12* | Acetone/$H_2O$ [1:1] | $K_2CO_3$ | 1.05 | 50 | 1 | 92 |
| *13* | Acetone/$H_2O$ (1:1) | $Na_2CO_3$ | 0.9 | 50 | 2.7 | 86 |
| *14* | Acetone/$H_2O$ [1:1] | $K_3PO_4$ | 0.9 | 50 | 1.2 | 70 |
| *15* | Acetone/$H_2O$ [1:1] | $Cs_2CO_3$ | 0.9 | 50 | 1.5 | 62 |
| *16* | Acetone/$H_2O$ [1:1] | $Et_3N$ | 0.9 | 50 | 24 | Trace |
| *17* | Acetone/$H_2O$ [1:1] | $K_2CO_3$ | 0.9 | 40 | 1 | 82 |
| *18* | Acetone/$H_2O$ [1:1] | $K_2CO_3$ | 0.9 | 25 | 1 | 57 |

[a]) Reaction conditions: benzoyl chloride (2.0 mmol), phenylboronic acid (1.0 mmol), base (2.5 mmol), solvent (4.0 ml). [b]) Yield of isolated products.

Scheme 1. Reaction of aroyl chloride (**1**) and arylboronic acid (**2**) in the presence of Pd(II)-salen@MWCNTs.

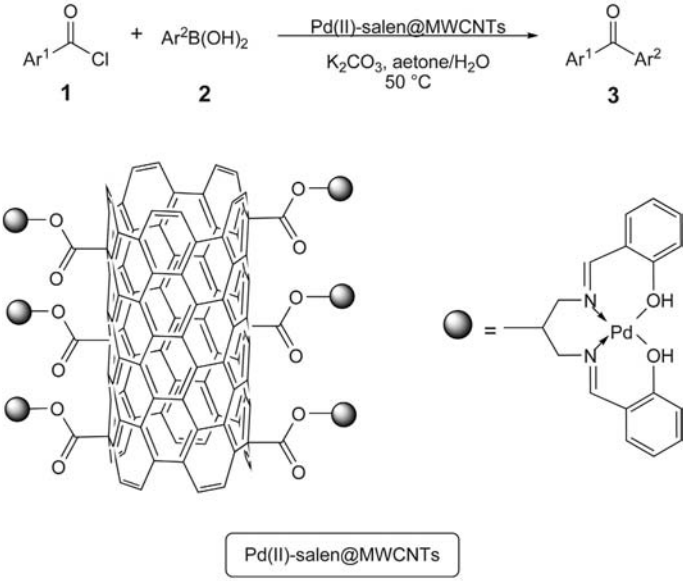


Table 2. Diaryl ketones from *Suzuki–Miyaura* coupling of aroyl chlorides and arylboronic acids[a])

| *Entry* | $Ar^1$ | $Ar^2$ | Time [h] | Yield [%][b]) | TON |
|---|---|---|---|---|---|
| *1* | $C_6H_5$ | $C_6H_5$ | 1 | 91 | 101 |
| *2* | 4-Me–$C_6H_4$ | $C_6H_5$ | 1.16 | 86 | 96 |
| *3* | 4-MeO–$C_6H_4$ | $C_6H_5$ | 1.5 | 83 | 92 |
| *4* | 4-$NO_2$–$C_6H_4$ | $C_6H_5$ | Immediately | 94 | 104 |
| *5* | 4-Cl–$C_6H_4$ | $C_6H_5$ | Immediately | 92 | 102 |
| *6* | 3-Cl–$C_6H_4$ | $C_6H_5$ | 0.83 | 75 | 83 |
| *7* | 2-F–$C_6H_4$ | $C_6H_5$ | 2 | 71 | 79 |
| *8* | 2-furoyl | $C_6H_5$ | 0.17 | 87 | 97 |
| *9* | 2-thenoyl | $C_6H_5$ | 0.17 | 81 | 90 |
| *10* | $C_6H_5$ | 4-$MeC_6H_4$ | 1 | 91 | 101 |
| *11* | $C_6H_5$ | 4-$MeOC_6H_4$ | 1 | 88 | 98 |

[a]) Reaction conditions: aroyl chloride (2.0 mmol), arylboronic acid (1.0 mmol), $K_2CO_3$ (2.5 mmol), Pd(II)-Salen@MWCNTs (0.9 mol-%) in acetone/$H_2O$ ($v/v$ = 1:1; 4.0 ml) at 50 °C. [b]) Yield of isolated products.

The reusability of the Pd(II)-salen@MWCNTs as the heterogeneous catalyst in the reaction of benzoyl chloride and phenylboronic acid was also investigated. The capability of recovery of the catalyst was confirmed after three successive runs with minimal loss of activity (*Fig.*). Furthermore, leaching of transition metal to solution during the course of a reaction is always an important issue for the heterogeneous catalysts, which directly affects the catalytic activity of these species. Therefore, the inductively coupled plasma (ICP) analysis was performed to determine the total leaching of Pd metal, and we found that 1.2% of Pd was lost after four reaction cycles in the above *Suzuki* coupling. So, lower yield of the coupling product in the fourth cycle can be attributed to the leaching of the Pd metal.

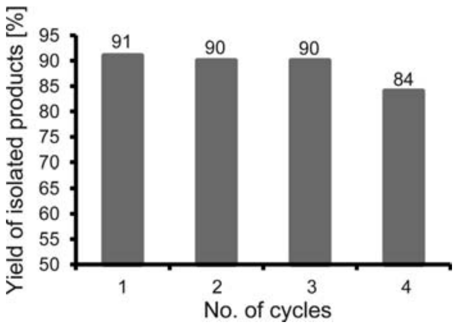


Figure. Reusability chart of the cross-coupling reaction of benzoyl chloride and phenylboronic acid.

A plausible catalytic mechanism for this cross-coupling reaction involves the following steps [16] (*Scheme 2*): *i*) preliminary reduction of Pd(II) precatalyst to active $L_nPd(0)$ by phenylboronic acid [29]; *ii*) oxidative addition of acyl chloride to the $L_nPd(0)$ species to

Scheme 2. Plausible mechanism for the cross-coupling reaction of aroyl chlorides and arylboronic acids.

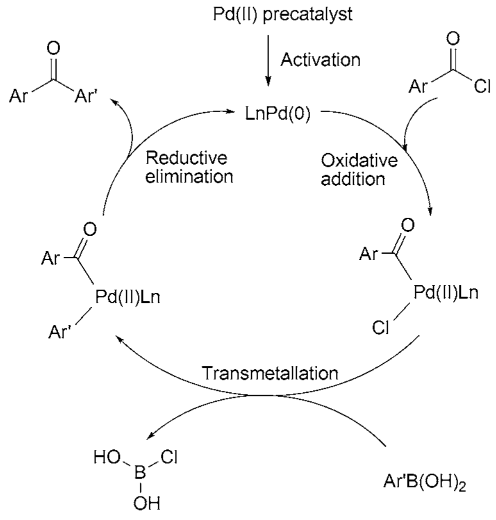


Table 3. Comparison of different catalytic systems with the present catalyst in the reaction between benzoyl chloride and phenylboronic acid

| *Entry* | Catalyst | Solvent | Time [h] | Temp. [°C] | Yield [%][a]) | TON |
|---|---|---|---|---|---|---|
| *1* | Pd(dba)$_2$ (5 mol-%) | Et$_2$O | 3 | 100 | 75 [13a] | 16 |
| *2* | PdCl$_2$(PPh$_3$)$_2$ (2 mol-%) | Toluene | 4 | 110 | 91 [30] | 45 |
| *3* | 'Si'-P-Pd(0) (3 mol-%) | Acetone/H$_2$O (3:1) | 12 | 60 | 93 [25] | 26 |
| *4* | Cyclopalladated ferrocenylimines (0.5 mol-%) | Toluene | 12 | 60 | 92 [31] | 196 |
| *5* | Pd(II)-salen@MWCNTs (0.9 mol-%) | Acetone/H$_2$O (1:1) | 1 | 50 | 91[b]) | 101 |

[a]) References are given in brackets. [b]) Present work.

generate acyl palladium(II) chloride complex; *iii*) transmetallation to transfer aryl group from B to the Pd center to produce Pd(II) complex which contain both the acyl and aryl substituents to be coupled; and *iv*) reductive elimination to yield the corresponding diaryl ketone.

Finally, we compared the performance of our reusable catalyst with other reported catalytic systems in the literature for the cross-coupling reaction of benzoyl chloride (**1a**) and phenylboronic acid (**2a**; *Table 3*). As shown in *Table 3*, the Pd-salen@MWCNTs exhibited superior catalytic activity in this transformation.

## Conclusion

In summary, we have demonstrated that Pd(II)-salen complex anchored to multiwalled carbon nanotubes could be conveniently used as a heterogeneous precatalyst for the efficient, general, phosphorous-free, and ecofriendly synthesis of aromatic ketones in aqueous media. In addition to the high catalytic activity, this precatalyst could be easily separated and reused for three consecutive cycles with consistent catalytic activity.

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## Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/hlca.201600161.

## Experimental Part

### General

All chemicals were purchased from *Merck* and *Aldrich* chemical companies. Melting points were determined on a *Büchi* melting point *B-540* apparatus. IR Spectra were recorded on an *ABB Bomem Model FTLA 2000* Spectrometer. NMR Spectra were recorded at 300 ($^1$H), and 75.5 ($^{13}$C) MHz, resp., on a commercial *Bruker DMX-300*, using CDCl$_3$ as a solvent.

The heterogeneous Pd(II)-salen@MWCNTs was characterized by transmission electron microscopy (TEM), attenuated total reflection infrared spectroscopy (ATR), *Raman* spectroscopy, inductively coupled plasma (ICP), thermogravimetric-differential thermal analysis (TG-DTA), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) techniques [28a]. The ATR spectrum of the catalyst showed a band at 1708 cm$^{-1}$ associated with C=O stretching of the ester linkage between the CNT and the *Schiff* base complex. The *Raman* spectrum showed four bands including tangential stretching G-band (1567 $cm^{-1}$), D-band (1331 $cm^{-1}$), second harmonic D*-band (2678 $cm^{-1}$), and radial breathing band (RBM, 288 $cm^{-1}$) which are characteristic of CNTs. Moreover, the metal content of the complex was found to be 16.20 ppm using ICP, and the ratio of Pd/N in the catalyst was obtained to be 1.82%. Further evidence for the modification of MWCNTs came from the XPS of the complex; the peaks at 290.8, 344.6, and 539.2 eV are attributed to C-, N-, and O-atom, respectively. Pd $3d_{3/2}$ and $3d_{5/2}$ peaks appear at 349.8 and 344.4 eV, respectively. Also, comparison between the TEM images of the purchased $CO_2H$-MWCNTs and Pd(II)-salen@MWCNTs confirmed the presence of the *Schiff* base complex. The XRD pattern of the catalyst confirmed the presence of graphite at around 26° and also the Pd metal at 39.9°, 47.4°, and 82.0°.

### *General Procedure for the* Suzuki–Miyaura *Cross-Coupling of Aroyl Chlorides*

A test tube was charged with Pd(II)-salen@MWCNTs (6 mg, 0.9 mol-%), acyl chloride (2.0 mmol), arylboronic acid (1.0 mmol), $K_2CO_3$ (2.5 mmol, 345.0 mg), acetone (2.0 ml), $H_2O$ (2.0 ml), and a magnetic stir bar. The mixture was stirred at 50 °C under air for appropriate time. The progress of the reaction was monitored using TLC. After completion of the reaction, the soln. was filtered; the catalyst was thoroughly washed with AcOEt (2 × 8 ml) and subjected to the next run. The combined org. phase was washed with 5% aq. $NaHCO_3$ (2 × 5 ml), and dried over $Na_2SO_4$. The solvent was then removed under reduced pressure. The product was further purified using prep. TLC ($SiO_2$) with hexane/AcOEt as an eluent.

### *Selected Spectral Data*

**4-Methylbenzophenone** (= **(4-Methylphenyl)(phenyl)methanone**; *Entry 2*, *Table 2*). Yield: 168 mg (86%). White solid. M.p. 50 – 53 °C. IR (KBr): 1657 (C=O). $^1$H-NMR (300 MHz, $CDCl_3$): 2.45 (*s*, Me); 7.27 – 7.31 (*m*, 2 arom. H); 7.46 – 7.51 (*m*, 2 arom. H); 7.56 – 7.59 (*m*, 1 arom. H); 7.72 – 7.75 (*m*, 2 arom. H); 7.78 – 7.81 (*m*, 2 arom. H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 21.6 (Me); 128.2 (CH); 129 (CH); 129.9 (CH); 130.3 (CH); 132.2 (CH); 134.8 (C); 137.9 (C); 143.2 (C); 196.5 (C=O).

**4-Methoxybenzophenone** (= **(4-Methoxyphenyl)(phenyl)methanone**; *Entry 3*, *Table 2*). Yield: 176 mg (83%). Pale yellow solid. M.p. 56 – 59 °C. IR (KBr): 1650 (C=O). $^1$H-NMR (300 MHz, $CDCl_3$): 3.88 (*s*, Me); 6.95 – 6.98 (*m*, 2 arom. H); 7.45 – 7.5 (*m*, 2 arom. H); 7.54 – 7.57 (*m*, 1 arom. H); 7.75 – 7.78 (*m*, 2 arom. H); 7.82 – 7.85 (*m*, 2 arom. H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 55.5 (Me); 113.5 (CH); 128.2 (CH); 129.7 (CH); 130.1 (CH); 131.9 (CH); 132.5 (C); 138.2 (C); 163.2 (C); 195.4 (C=O).

**(2-Fluorophenyl)(phenyl)methanone** (*Entry 7, Table 2*). Yield: 142 mg (71%). Yellow oil. IR (neat): 1668 (C=O). $^1$H-NMR (300 MHz, $CDCl_3$): 7.15 – 7.20 (*m*, 1 arom. H); 7.23 – 7.31 (*m*, 1 arom. H); 7.45 – 7.65 (*m*, 5 arom. H); 7.80 – 7.87 (*m*, 2 arom. H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 116.24 (*d*, *J*(C,F) = 21.7, CH); 124.2 (*d*, *J*(C,F) = 3.5, CH); 127.0 (*d*, *J*(C,F) = 14.9, C); 128.4 (CH); 129.8 (CH); 130.85 (*d*, *J*(C,F) = 2.93, CH); 133.03 (*d*, *J*(C,F) = 8.2, CH); 133.4 (CH); 137.3 (C); 160.04 (*d*, *J*(C,F) = 50.8, C); 193.5(C=O).

**Furan-2-yl Phenyl Ketone** (= **Furan-2-yl(phenyl)methanone**; *Entry 8, Table 2*). Yield: 150 mg (87%). Yellow oil. IR (neat): 1647 (C=O). $^1$H-NMR ($CDCl_3$, 300 MHz): 6.59 (*dd*, *J* = 3.5, 1.7, 1 arom. H); 7.23 – 7.27 (*m*, 1 arom. H); 7.47 – 7.52 (*m*, 2 arom. H); 7.57 – 7.60 (*m*, 1 arom. H); 7.71 (*d*, *J* = 1, 1 arom. H); 7.95 – 7.98 (*m*, 2 arom. H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): 112.2 (CH); 120.6 (CH); 128.4 (CH); 129.2 (CH); 132.6 (CH); 137.2 (C); 147.1 (CH); 152.2 (C); 182.6 (C=O).

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