drick, SHELXTL/PC, Version 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, WI, (USA)). b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-103167. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[13] In the presence of $CuPF_6$/**1**, addition of ethyl diazoacetate to propargyl methyl ether formed the product from cyclopropenation in 81% *ee* (60% yield).

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## A Novel Method for the Demetalation of Tricarbonyliron–Diene Complexes by a Photolytically Induced Ligand Exchange Reaction with Acetonitrile**

Hans-Joachim Knölker,* Helmut Goesmann, and Rüdiger Klauss

Tricarbonyl($\eta^4$-1,3-diene)iron complexes are a useful class of organometallic compounds with versatile applications to organic synthesis.[1] The coordination of the conjugated diene to the transition metal fragment leads to a significant alteration of its reactivity. Therefore, the tricarbonyliron fragment has been used for the stabilization of labile hydrocarbons and as a protecting group for dienes.[1] After the desired transformations at the ligand of the tricarbonyl($\eta^4$-1,3-diene)iron complex a demetalation is required to provide the free diene. This decomplexation of tricarbonyliron complexes is usually achieved under strong oxidizing reaction conditions, for example with ferric chloride,[2] ceric ammonium nitrate,[3] trimethylamine *N*-oxide (TMANO),[4] cupric chloride,[5] or hydrogen peroxide/sodium hydroxide.[6] In connection with investigations of the iron-mediated [2+2+1] cycloaddition[7, 8] and our studies directed towards the application of tricarbonyliron complexes to the synthesis of alkaloids[9] we required a method for demetalation of tricarbonyliron complexes by using extremely mild reaction conditions. Herein we describe a novel procedure for the demetalation of tricarbonyliron–diene complexes using a photolytically induced exchange of the carbonyl ligands by acetonitrile at low temperature and subsequent demetalation in the air.

Although the iron-mediated [2+2+1] cycloaddition has been known for four decades,[10] only a few very limited applications were reported because of the difficulties associated with the demetalation of the resulting tricarbonyl($\eta^4$-cyclopentadienone)iron complexes. We recently demonstrated that selective demetalation is feasible using trimethylamine *N*-oxide by careful control of the reaction conditions.[7a,b] However, the yields in some cases were only moderate. Therefore, we set out to develop a novel demetalation procedure in which the bonding of the metal fragment to the diene becomes labile by exchange of the carbon monoxide ligands. Acetonitrile ligands appeared to be promising candidates for such a transformation in the coordination sphere of the metal since they are rather poor acceptors. Thus, their introduction should result in a decreased back donation of electrons from the filled iron d orbitals to the ligand and the resulting complexes should be more easily oxidized.

The tricarbonyliron complex **1a**[7a] is stable at room temperature in the air. No acetonitrile complexes are observed on refluxing a solution of **1a** in acetonitrile for 29 h in the dark. However, exposure to daylight at room temperature results in a very slow formation of the monoacetonitrile complex **2a** along with the demetalated cyclopentadienone **5a**. Irradiation of a solution of complex **1a** in acetonitrile under argon atmosphere using a medium-pressure mercury lamp accelerates the ligand exchange dramatically and leads to a stepwise exchange of all three carbonyl ligands (Scheme 1, Table 1).

Photolysis of **1a** in acetonitrile at −30 °C afforded after 1 h the diacetonitrile complex **3a** in 76% as dark red crystals. Injection of argon into the solution during the photolysis provided a purple solution of the triacetonitrile complex **4a**. The addition of the third acetonitrile ligand is reversible even at −30 °C. Therefore, the complexes **3a** or **4a** can be prepared selectively. In order to prove the reversibility of the ligand exchange carbon monoxide was injected at −30 °C into the purple solution of complex **4a** in acetonitrile. Within 30 min the color changed to red and the diacetonitrile complex **3a** was isolated in 65% yield based on **1a**. On warming the mixture, the exchange of the second acetonitrile ligand becomes reversible too. By injection of carbon monoxide at room temperature the red solution turned orange and the monoacetonitrile complex **2a** was obtained in 61% yield based on **1a**. Related ligand exchange reactions at the cationic complex $[\eta^5\text{-CpFe(CO)}_3]^+PF_6^-$ were previously described by Astruc et al.[11] However, the cationic CpFe complexes with acetonitrile ligands reported therein are fairly stable compared to those of cyclopentadienones.

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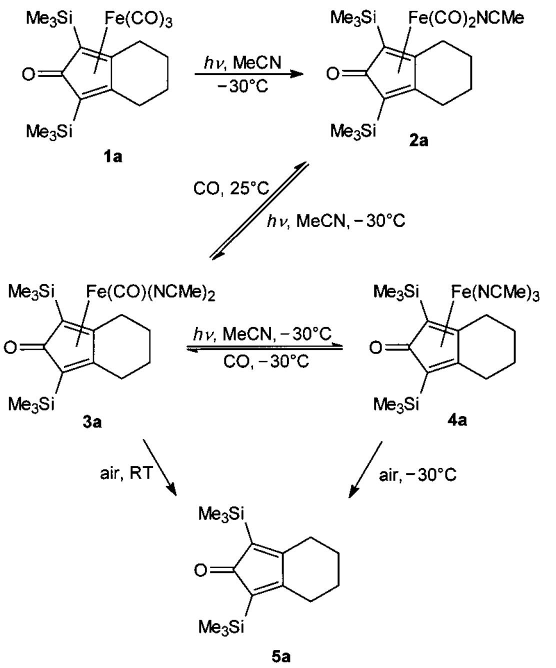


Scheme 1. Photolytically induced ligand exchange reactions at complex **1a** with acetonitrile and demetalation of the resulting acetonitrileiron complexes **3a** and **4a**.

Table 1. Demetalation of the (cyclopentadienone)iron complexes **1a**–**4a** by stirring of an acetonitrile solution in the air.

| Complex | $\tilde{\nu}_{C=O}$ [cm$^{-1}$] | Reaction conditions | **1a**, Yield [%] | **2a**, Yield [%] | **5a**, Yield [%] |
|---|---|---|---|---|---|
| **1a** | 1606 | 25 °C, 3 h | 96 | 1 | 2 |
| **1a** | 1606 | 25 °C, 70 h | 87 | 5 | 5 |
| **2a** | 1589 | 25 °C, 24 h | – | 60 | 39 |
| **3a** | 1544 | 25 °C, 1 h | – | – | 100 |
| **4a** | 1510 | −30 °C, 1–2 min[a] | – | – | (quant.) |

[a] Demetalation by injection of air into the solution of complex **4a** without isolation.

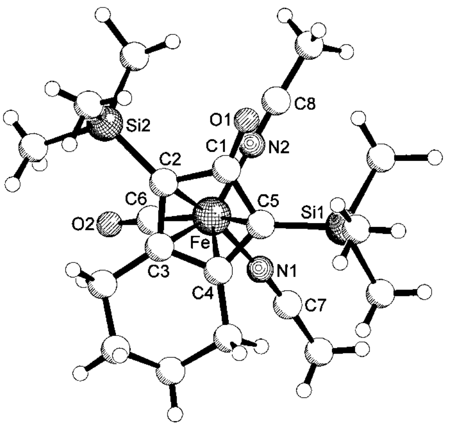


Figure 1. Molecular structure of **3a** in the crystal. Selected bond lengths [Å]: Fe–C2 2.114(9), Fe–C3 2.057(9), Fe–C4 2.053(9), Fe–C5 2.131(9), Fe–C6 1.758(11), Fe–N1 1.942(9), Fe–N2 1.940(8), C1–O1 1.237(10), C6–O2 1.155(10), N1–C7 1.147(12), N2–C8 1.145(12).

The structural assignments of the complexes **2a** and **3a** are based on their spectral data[12] and an X-ray crystal structure determination of **3a** (Figure 1).[13] A characteristic structural feature of the diacetonitrile complex **3a** is the loss of symmetry caused by exchange of the second carbonyl ligand. In contrast the complexes **1a**[7a] and **2a** are symmetrical. The $^{1}$H and $^{13}$C NMR spectra show the unsymmetrical arrangement of the coligands of complex **3a** in solution by the loss of $C_S$ symmetry. The X-ray analysis confirms the conformation of the metal fragment for the solid state with tetragonal-pyramidal coordination of the iron atom and one acetonitrile ligand in the apical position (Figure 1). The $^{13}$C NMR spectrum in deuterated [D$_8$]dioxane at room temperature exhibits sharp signals for all carbon atoms indicating that the preferred conformation is frozen under these conditions. Stepwise increase of the temperature using [D$_{10}$]$p$-xylene as solvent leads to coalescence of the two signals for the trimethylsilyl (TMS) groups in the $^{1}$H NMR spectrum at 400 MHz. The activation barrier for this fluxional process caused by basal–apical ligand exchange was determined (Figure 2).[14] The free enthalpies of activation for related turnstile rotations of several tricarbonyliron–diene complexes were previously reported.[15] The activation barrier for the intramolecular ligand exchange at the present (diacetonitrile)carbonyliron fragment of **3a** was found to be $\Delta G^{\neq} = 17.0 \pm 0.3$ kcal mol$^{-1}$ ($T_C = 334 \pm 5$ K, $\Delta\nu =$ 18 Hz). This value is significantly higher than observed for the tricarbonyliron complexes of cyclohexa-1,3-diene ($\Delta G^{\neq} =$ $8.7 \pm 0.3$ kcal mol$^{-1}$),[15e] buta-1,3-diene ($\Delta G^{\neq} = 10.5 \pm 0.5$ kcal mol$^{-1}$),[15c] and even 1-azabuta-1,3-dienes ($\Delta G^{\neq} = 13.5$–$14.7 \pm 0.3$ kcal mol$^{-1}$),[15e] and indicates a reduced back bonding from the iron atom to the acetonitrile coligands. On the other hand, the stretching frequency for the carbonyl band of the carbon monoxide ligand of complex **3a** at 1926 cm$^{-1}$ is much lower than for the corresponding tricarbonyliron complex **1a**,[7a] which is significant of an increased back donation of electrons from iron d orbitals into the LUMO of the carbonyl ligand. Due to its high sensitivity the triacetonitrile complex **4a** could be characterized only by FT-IR spectroscopy.[12] The IR spectra show decreasing stretching frequencies for the carbonyl bands of the cyclopentadienone with increasing donor substitution at the metal (Table 1). A similar shift is observed for the C≡N bands of the complexes **3a** and **4a**.

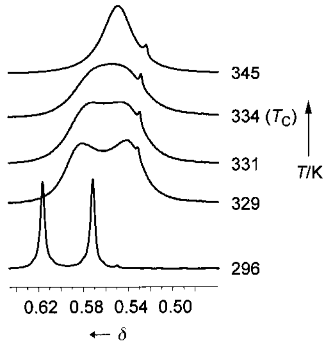


Figure 2. Dynamic $^{1}$H NMR spectra of complex **3a** in the TMS region (400 MHz, [D$_{10}$]$p$-xylene).

We next investigated the demetalation behavior of the complexes **1a**–**4a**. The orange yellow complex **2a** is stable at room temperature and the crystals can be handled even in the air. A solution of **2a** undergoes a selective demetalation in the air to provide the free ligand **5a** (see Table 1). However, even after 24 h there is still 60 % of complex **2a** unchanged. The diacetonitrile complex **3a** can be stored at room temperature under inert gas atmosphere. Injection of air into the solution of **3a** in acetonitrile at −30 °C does not lead to demetalation. However, on stirring the solution of complex **3a** in the air at room temperature the red color disappears completely within 1 h and the cyclopentadienone **5a** can be isolated quantitatively. The triacetonitrile complex **4a** is extremely air sensitive. Solutions of complex **4a** in acetonitrile are stable only under argon atmosphere at temperatures below −20 °C. Warming the cold solution of **4a** leads to decomposition. However, the solid compound can be handled at room temperature under an argon atmosphere for a short period of time. On injection of air into a solution of **4a** in acetonitrile at −30 °C the purple color of the triacetonitrile complex disappears instantaneously and the free ligand **5a** is obtained in excellent yield. The differences of the complexes **3a** and **4a** with respect to their stability in the air can be utilized for a chemoselective demetalation which was monitored by FT-IR spectroscopy (Figure 3). Photolysis of **1a** in acetonitrile at −30 °C with injection of argon into the solution, evaporation of the solvent at −20 °C, and washing of the residue with hexane provides the triacetonitrile complex **4a** along with the diacetonitrile complex **3a** as minor product. Brief contact of the solid complexes to the air leads to instantaneous demetalation of **4a** to the free ligand **5a** (IR band at 1678 cm$^{-1}$), while **3a** is stable under these conditions.

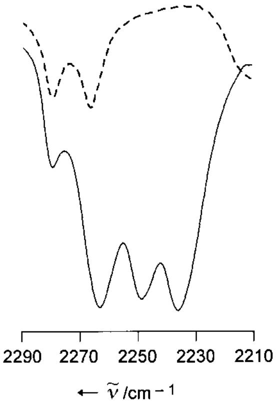
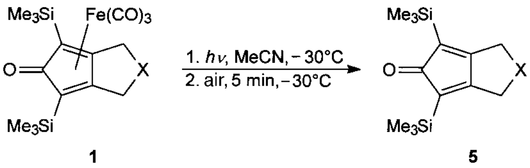


Figure 3. IR spectrum of the triacetonitrileiron complex **4a** containing the diacetonitrileiron complex **3a** (solid line); IR spectrum after contact with air for 3 s (dotted line).

The feasibility to focus the reaction on **3a** or **4a**, respectively, offers two alternative pathways for the demetalation by photolytically induced ligand exchange. Method A: photolysis of **1a** in acetonitrile at −30 °C with injection of argon into the solution for 45 min and subsequent demetalation of the intermediate triacetonitrile complex **4a** by injection of air at −30 °C. Method B: photolysis of **1a** in acetonitrile at −30 °C under argon atmosphere (but without injection of argon into the solution!) for 60 min and demetalation of the intermediate diacetonitrile complex **3a** by injection of air with simultaneous warming to room temperature. The cyclopentadienone **5a** was provided in 89 % yield by method A and in 88 % yield by method B. The demetalation of a series of bicyclic tricarbonyl($\eta^4$-cyclopentadienone)iron complexes **5** was carried out using method A with individual optimization of the irradiation time if necessary (Scheme 2, Table 2). The yields for the free ligands **5a–d**, previously prepared by using TMANO,[7b] were considerably improved (83–91 %). The cyclopentadienone **5e** could be obtained for the first time by the present method.[16] Treatment of **5e** with TMANO led to the known thiophene derivative by twofold double-bond isomerization and protodesilylation. This result provides direct evidence for the sequence of steps involved in the demetalation of **1e** with TMANO.[7b]



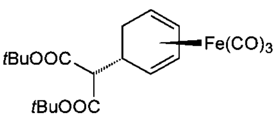
Scheme 2. Photolysis of the tricarbonyliron complexes **1** in acetonitrile with subsequent demetalation of the intermediate triacetonitrileiron complexes by injection of air.

Table 2. Demetalation of the bicyclic tricarbonyl($\eta^4$-cyclopentadienone)iron complexes **1** via the intermediate triacetonitrile complexes **4** (method A).

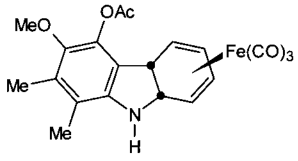
| **1** | X | Irradiation time [min] | **5**, Yield [%] |
|---|---|---|---|
| **a** | $(CH_2)_2$ | 45 | 89 |
| **a** | $(CH_2)_2$ | 60 | 88[a] |
| **b** | $CH_2$ | 45 | 91 |
| **c** | $C(COOMe)_2$ | 45 | 86 |
| **d** | O | 60 | 83 |
| **e** | S | 30 | 56 |

[a] Method B: Demetalation via the diacetonitrile complex **3a**.

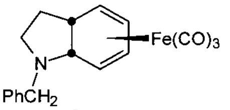
Moreover, the novel demetalation procedure was also applied to the tricarbonyl($\eta^4$-cyclohexa-1,3-diene)iron complexes **6–8** [17] and the ($\eta^4$-buta-1,3-diene)tricarbonyliron complex **9**. The irradiation time for the cyclohexadiene and butadiene complexes was increased to 90 min in order to achieve a complete ligand exchange. Using method B via the intermediate diacetonitrile complexes the free dienes **6a–9a** were obtained in high yields (80–85 %). The reaction sequence for the demetalation of tricarbonyliron complexes of cyclohexa-1,3-dienes and buta-1,3-dienes is most likely the same as described above for cyclopentadienone complexes. However, the acetonitrileiron complexes of simple dienes are much more labile than their cyclopentadienone analogues. Photolysis of complex **6** in acetonitrile at −30 °C led to the exchange of two carbonyl ligands. The resulting diacetonitrile complex was characterized by IR spectroscopy by the two bands in the C≡N region (2310 and 2282 cm$^{-1}$) and demetalated within a few minutes on contact with air. Method A via an intermediate triacetonitrile complex provided a better result for the demetalation of the cyclohexadiene complex **6** (yield of **6a**: 87 %). The demetalation of **7** to **7a** [18] by photolytically induced ligand exchange using method B provided the first example of a 4a,9a-dihydro-9*H*-carbazole unsubstituted at the nitrogen atom which is not coordinated to a metal atom.[19]



**6**



**7**



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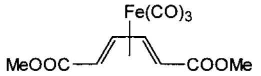

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In conclusion, we developed a novel procedure for the demetalation of tricarbonyl($\eta^4$-1,3-diene)iron complexes under very mild reaction conditions. It could be demonstrated that the present procedure provides access to free ligands not available by previous methods.

## *Experimental Section*

General procedure for the demetalation of the bicyclic tricarbonyl($\eta^4$-cyclopentadienone)iron complexes **1** by photolytically induced ligand exchange (method A): A solution of complex **1** (0.239 mmol) in acetonitrile (120 mL) was photolyzed using a 150 W medium-pressure mercury lamp (Heraeus TQ 150, Pyrex filter) at $-30\,^{\circ}C$ for 30–60 min (see Table 2) with concomitant injection of argon into the solution. Then air was injected into the cold purple solution for 5 min. Filtration through a short path of Celite, evaporation of the solvent, and flash chromatography of the residue on silica gel provided the free ligand **5**.

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[12] Spectral data of the mono-, di-, and triacetonitrileiron complexes **2a**, **3a**, and **4a**. **2a**: Diffuse reflectance infrared Fourier transform (DRIFT)-IR: $\tilde{\nu} = 2944$, 2899, 2865, 1987, 1932, 1589, 1441, 1394, 1374, 1367, 1342, 1261, 1244 $cm^{-1}$; $^1H$ NMR (400 MHz, $C_6D_6$): $\delta = 0.45$ (s, 18H), 0.86 (s, 3H), 1.26 (m, 4H), 2.09 (m, 2H), 2.35 (m, 2H); $^{13}C$ NMR and DEPT (100 MHz, $CDCl_3$): $\delta = -0.12$ (6 $CH_3$), 4.46 ($CH_3$), 22.30 (2 $CH_2$), 24.82 (2 $CH_2$), 69.92 (2 C), 106.57 (2 C), 126.07 ($C{\equiv}N$), 180.09 ($C{=}O$), 212.83 (2CO); elemental analysis calcd for $C_{19}H_{29}FeNO_3Si_2$ (%): C 52.89, H 6.77, N 3.25; found: C 52.86, H 6.67, N 2.90. **3a**: DRIFT-IR: $\tilde{\nu} =$ 3823, 2950, 2279, 2266, 1926, 1544, 1443, 1406, 1370, 1300, 1267, 1239, 1071 $cm^{-1}$; $^1H$ NMR (400 MHz, $C_6D_6$): $\delta = 0.53$ (s, 9H), 0.55 (s, 9H), 0.69 (s, 3H), 1.27 (s, 3H), 1.52 (m, 1H), 1.64 (m, 2H), 1.74 (m, 1H), 1.89 (m, 1H), 2.12–2.27 (m, 2H), 2.67 (m, 1H); $^{13}C$ NMR and DEPT (125 MHz, $[D_8]$dioxane): $\delta = 0.19$ (3$CH_3$), 0.65 (3$CH_3$), 3.46 ($CH_3$), 3.75 ($CH_3$), 23.41 ($CH_2$), 23.65 ($CH_2$), 25.20 ($CH_2$), 25.80 ($CH_2$), 46.29 (C), 70.47 (C), 98.16 (C), 102.53 (C), 127.05 ($C{\equiv}N$), 129.15 ($C{\equiv}N$), 178.41 ($C{=}O$), 218.74 (CO); elemental analysis calcd for $C_{20}H_{32}FeN_2O_2Si_2$ (%): C 54.04, H 7.26, N 6.30; found: C 53.83, H 7.20, N 6.15. **4a**: DRIFT-IR: $\tilde{\nu} = 2263$, 2249, 2236, 1510 $cm^{-1}$.

[13] X-ray crystal structure analysis of **3a**: $C_{20}H_{32}FeN_2O_2Si_2$, orthorhombic, space group *Pbca*, $a = 9.583(6)$, $b = 18.102(14)$, $c = 27.40(2)$ Å, $V = 4753(6)$ Å$^3$, $Z = 8$, $T = 200(2)$ K, $\rho_{calcd} = 1.242\ g\,cm^{-3}$, $\mu = 0.751\ mm^{-1}$, $\lambda = 0.71073$ Å, $\theta$ range: 2.25–20.00°; 2205 independent reflections; refinement method: full-matrix least squares on $F^2$; final $R$ indices $[I > 2\sigma(I)]$: $R_1 = 0.0674$, $wR_2 = 0.0960$, maximal residual electron density: 0.378 e Å$^{-3}$. Programs: G. M. Sheldrick, SHELXS-86 (Göttingen **1986**), SHELXL-93 (Göttingen **1993**); E. Keller, SCHAKAL-97 (Freiburg i.Br., **1997**). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103176. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[16] **5e**: m.p. 89–90 °C; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 0.18$ (s, 18H), 3.71 (s, 4H); $^{13}C$ NMR and DEPT (125 MHz, $CDCl_3$): $\delta = -0.83$ (6$CH_3$), 30.40 (2$CH_2$), 125.21 (2C), 173.32 (2C), 211.96 ($C{=}O$); elemental analysis calcd for $C_{13}H_{22}OSSi_2$ (%): C 55.26, H 7.85; found: C 55.21, H 7.84.

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[18] **7a**: m.p. 113 °C; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 2.03$ (s, 3H), 2.15 (s, 3H), 2.35 (s, 3H), 3.59 (br s, 1H), 3.67 (s, 3H), 4.12 (br d, $J = 12.0$ Hz, 1H), 4.50 (dd, $J = 12.0$, 4.8 Hz, 1H), 5.70 (ddt, $J = 9.7$, 3.3, 0.9 Hz, 1H), 5.81 (ddd, $J = 9.7$, 4.8, 0.9 Hz, 1H), 5.90 (m, 1H), 6.00 (ddd, $J = 9.7$, 5.2, 0.4 Hz, 1H); $^{13}C$ NMR and DEPT (125 MHz, $CDCl_3$): $\delta = 12.38$ ($CH_3$), 13.90 ($CH_3$), 20.62 ($CH_3$), 40.25 (CH), 55.16 (CH), 61.00 ($CH_3$), 117.16 (C), 120.85 (C), 121.66 (CH), 124.07 (CH), 124.36 (CH), 125.98 (CH), 129.74 (C), 138.78 (C), 143.42 (C), 145.32 (C), 169.05 ($C{=}O$); elemental analysis calcd for $C_{17}H_{19}NO_3$ (%): C 71.56, H 6.71, N 4.91; found: C 71.47, H 6.80, N 4.87.

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