

# Synthesis and Structural Studies of Group 2B Transition Metal Complexes with the Bulky Nitrogen Ligand Bis[*N*-(2,6-diisopropylphenyl) imino]acenaphthene

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**Summary.** Group 2B transition metal complexes of bis[*N*-(2,6-diisopropylphenyl)imino]acenaphthene (*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-BIAN), namely, [Hg(*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-BIAN)Cl<sub>2</sub>] (**1**), [Zn(*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-BIAN)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**2**), and [Cd(*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-BIAN)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**3**) have been synthesized and characterized. In complexes **2** and **3**, IR, NMR, and conductivity measurements confirm the coordination of two (*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-BIAN) ligands to the metal center with two discrete perchlorate anions. X-Ray crystal structure of **1** indicates a distorted tetrahedral geometry with two nitrogen atoms from (*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-BIAN) ligand and two chloride atoms coordinating to the Hg(II) center.

**Keywords.** N-Ligands; X-Ray structure determination; Group 2B transition metal complexes.

## Introduction

Metal diimine complexes have been extensively studied in the past 20 years [1]. Special attention has focused on their applications in solar energy conversions, supramolecular assemblies, photocatalysis, nonlinear optics, photonic devices, and photoluminescent probes of biological systems [2–5].

Rigid bidentate ligand bis[*N*-(2,6-diisopropylphenyl)imino]acenaphthene (*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-BIAN) is regarded as a diimine containing two conjugated imine functions [6]. The presence of two exocyclic imines which are not part of the heterocyclic ring system, is leading to better  $\sigma$ -donating and better  $\pi$ -accepting properties. This property allows the ligand to stabilize both the higher and lower oxidation states of the metal ions. Another interesting property of (*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-

*BIAN*) ligand is the rigidity of the acenaphthene backbone which forces the imine N-atoms to remain in a fixed *cis* orientation, favoring a chelating coordination to a metal center.

In this paper we discuss the synthesis and full characterization of three complexes namely,  $[\text{Hg}(o,o'-i\text{Pr}_2\text{C}_6\text{H}_3\text{-BIAN})\text{Cl}_2]$  (**1**),  $[\text{Zn}(o,o'-i\text{Pr}_2\text{C}_6\text{H}_3\text{-BIAN})_2](\text{ClO}_4)_2$  (**2**) and  $[\text{Cd}(o,o'-i\text{Pr}_2\text{C}_6\text{H}_3\text{-BIAN})_2](\text{ClO}_4)_2$  (**3**). X-Ray crystal structure of **1** will also be presented and compared with the structure of the free (*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN*) ligand [6].

## Results and Discussion

### Crystal Structure Analysis of $[\text{Hg}(o,o'-i\text{Pr}_2\text{C}_6\text{H}_3\text{-BIAN})\text{Cl}_2]$ (**1**)

The ORTEP plot with the atomic-numbering scheme of  $[\text{Hg}(o,o'-i\text{Pr}_2\text{C}_6\text{H}_3\text{-BIAN})\text{Cl}_2]$  is depicted in Fig 1. Selected bond lengths, angles, and torsion angles are compiled in Table 1. As expected, the bulky ligand inhibits any tendency to polymer formation and only distorted tetrahedral monomer structure is observed with two imine nitrogen atoms and two chloride atoms coordinated to Hg(II) ion. The dihedral angle between the Cl–Hg–Cl and N–Hg–N tetrahedral planes is 70.45°. Tetrahedral complexes containing the HgN<sub>2</sub>X<sub>2</sub> group (X = halogen) tend to display rather large X–Hg–X angles, with associated lengthening of the average N–Hg bond lengths [7]. In **1**, the angle Cl(2)–Hg(1)–Cl(1) and the average N–Hg bond length, are 141.46(13)° and 2.473(4) Å, respectively. The mean Hg–Cl distance of 2.324(2) Å is typical for chloro complexes of Hg(II), as many compounds containing Hg(II)–Cl bonds (for the terminal chloride) were found to have an average distance of 2.42(12) Å [8, 9]. Larger Hg–Cl bond distances are always found in compounds where the chlorides are bridging, or hydrogen bonded, or

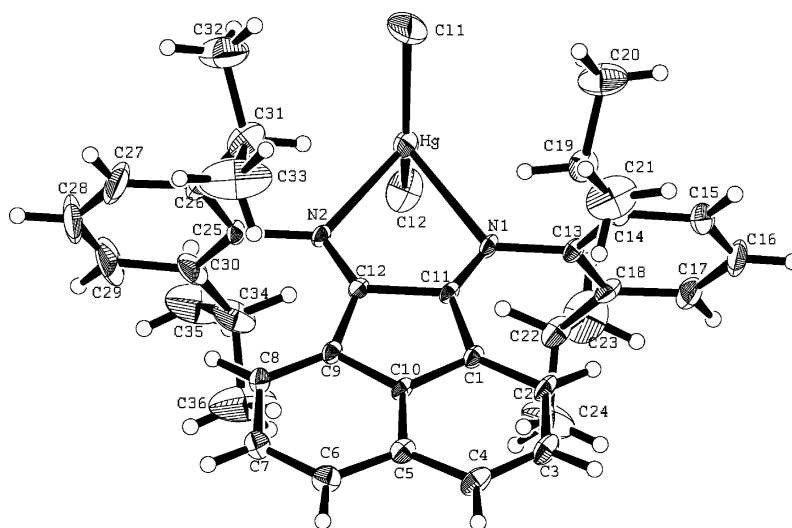


Fig. 1. ORTEP view of  $[\text{Hg}(o,o'-i\text{Pr}_2\text{C}_6\text{H}_3\text{-BIAN})\text{Cl}_2]$

**Table 1.** Selected bond lengths [Å], angles [°], and torsion angles [°] for [Hg (*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN*)Cl<sub>2</sub>]

Hg(1)–Cl(1)	2.330(2)	Cl(2)–Hg(1)–Cl(1)	141.46(13)
Hg(1)–Cl(2)	2.319(2)	Cl(2)–Hg(1)–N(1)	103.76(14)
Hg(1)–N(1)	2.462(5)	Cl(1)–Hg(1)–N(1)	107.46(12)
Hg(1)–N(2)	2.484(4)	Cl(2)–Hg(1)–N(2)	108.33(14)
N(1)–C(11)	1.269(7)	Cl(1)–Hg(1)–N(2)	103.50(11)
N(1)–C(13)	1.431(6)	N(1)–Hg(1)–N(2)	69.32(14)
N(2)–C(12)	1.273(7)	N(1)–C(11)–C(12)–N(2)	–3.71(0.67)
N(2)–C(25)	1.423(6)	C(1)–C(11)–C(12)–C(9)	–2.04(0.47)
C(11)–C(12)	1.520(6)	C(11)–N(1)–C(13)–C(14)	–97.65(0.66)
C(11)–N(1)–C(13)	119.9(5)	C(11)–N(1)–C(13)–C(18)	89.58(0.64)
C(12)–N(2)–C(25)	121.3(4)	C(12)–N(2)–C(25)–C(30)	–81.06(0.62)
C(2)–C(1)–C(10)	118.7(5)	C(12)–N(2)–C(25)–C(26)	100.16(0.57)
N(1)–C(11)–C(1)	132.7(5)	C(1)–C(11)–C(12)–N(2)	176.83(0.40)
N(1)–C(11)–C(12)	120.7(5)	C(1)–C(11)–C(12)–C(9)	–2.04(0.47)
C(1)–C(11)–C(12)	106.6(4)	N(1)–C(11)–C(12)–C(9)	177.42(0.43)

weakly bonded in a polymeric structures [10, 11]. In **1**, much smaller Hg–Cl bond distance also explains for the longer N–Hg bond length.

A comparison with free ligand (*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN*) shows a less planar bis(imino)acenaphthene skeleton as confirmed by bigger torsion angles (N(1)–C(11)–C(12)–N(2) –3.71 (0.67)° and C(1)–C(11)–C(12)–C(9) –2.04 (0.47)°). The corresponding angles of *o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN* ligand are –0.79 (0.29)° and –1.70 (0.21)°, respectively. The angle between the planes of naphthalene backbone and the aromatic N substituents, C(11)–N(1)–C(13)–C(14), is more perpendicular in [Hg(*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN*)Cl<sub>2</sub>] (about 82°) than in the free (*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN*) ligand (about 76°). This must be ascribed to the *o*-isopropyl substituents on the aromatic groups, rather than to the coordination to mercury.

### IR Spectra of Complexes

Infrared spectral data for the free *o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN* ligand and complexes **1–3** are listed in Table 2. Bands assigned to C=N stretching vibrations of the ligand

**Table 2.** Infrared and electrical conductivity data of complexes **1–3** at room temperature

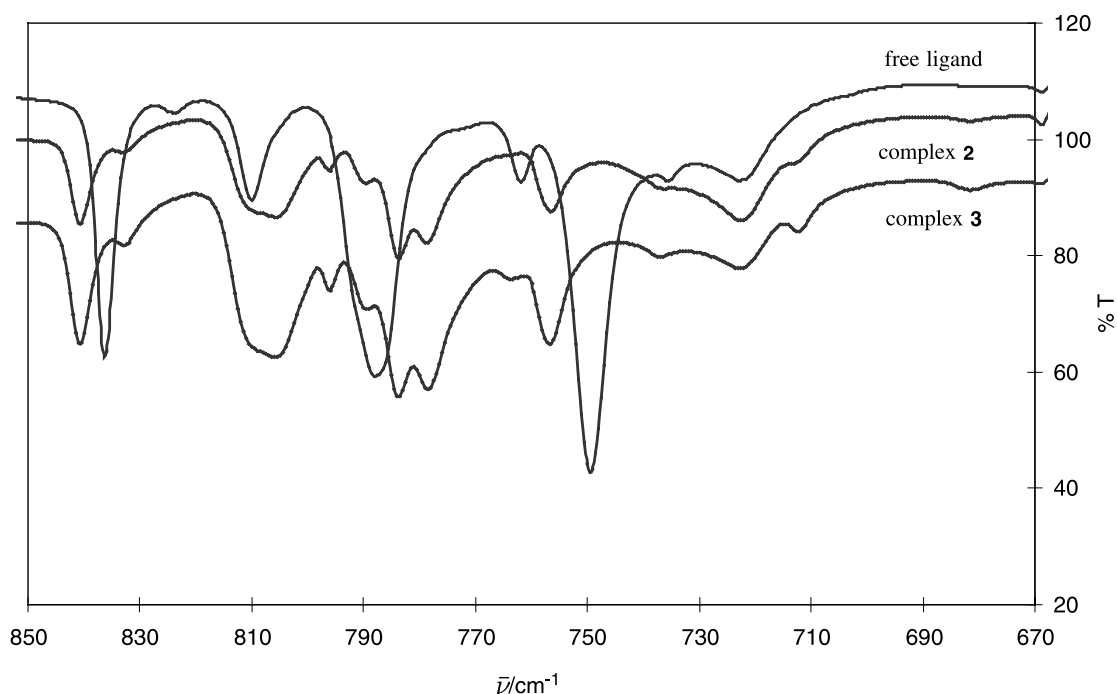
Compound	$\bar{\nu}(\text{C}=\text{N})$	$\bar{\nu}(\text{ClO}_4^-)$	$A_m/\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	
	cm <sup>-1</sup>	cm <sup>-1</sup>	AN	NM
( <i>o,o'</i> - <i>iPr</i> <sub>2</sub> C <sub>6</sub> H <sub>3</sub> - <i>BIAN</i> )	1671, 1652, 1642	–	–	–
<b>1</b>	1668, 1626	–	27	4.6
<b>2</b>	1668, 1634	1110, 620	290	175
<b>3</b>	1666, 1629	1108, 620	300	180

were observed in the  $1642\text{--}1671\text{ cm}^{-1}$  range. These bands are shifted to lower wavenumbers in complexes spectra indicating the coordination of both diimine nitrogen atoms of *o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-BIAN ligand to the metal ion.

In perchlorate complexes **2** & **3**, a strong band observed at around  $1110\text{ cm}^{-1}$  (antisymmetric stretch) and the sharp band at  $620\text{ cm}^{-1}$  (antisymmetric bend) suggest uncoordinated perchlorate anions [12]. Conductivity measurements (Table 2) in AN (acetonitrile) and NM (nitromethane) confirm that ClO<sub>4</sub><sup>-</sup> acts only as a counter ion and does not coordinate with any complex cation [13].

Generally, it is known that the aromatic rings with three adjacent free hydrogen atoms show strong bands in the  $810\text{--}750\text{ cm}^{-1}$  region due to the out-of-plane CH deformation vibrations [14]. Their position is determined almost completely by their location on the ring rather than by the nature of the substituent and, with certain limitations, they provide an excellent method for recognition of the type of substitution. The very high intensity and sensitivity of these characteristic bands in this region make them particularly well suited for quantitative work, too. The splitting of these out-of-plane CH deformation vibrations bands of the complexes in the  $810\text{--}750\text{ cm}^{-1}$  region (Fig. 2) can be considered as a sign of the coordination of two *Ar*-BIAN ligands to the metal ion [15].

In **1**, the Cl–Hg–Cl stretching frequency and the structural modifications induced in the HgCl<sub>2</sub> molecule can be taken as an indication of the strength of the metal-ligand interaction. The higher charge density on the mercury atom due to coordination of diimine nitrogen atoms weakens the Hg–Cl bonds, thus producing a shift of  $\bar{\nu}(\text{Cl}\text{--}\text{Hg}\text{--}\text{Cl})$  towards lower wavenumber and a lengthening of the Hg–Cl



**Fig. 2.** IR spectra of free ligand and complexes **2** & **3** in the  $850\text{--}670\text{ cm}^{-1}$  region

distance. The Hg–Cl mean distance is 2.33 Å compared to the value of 2.291(9) Å in free HgCl<sub>2</sub> [16], the wavenumber of the IR Cl–Hg–Cl stretching frequency is 348 compared to 378 cm<sup>-1</sup> [17].

In conclusion, the crystal structure of complex **1** indicates a distorted tetrahedral monomer structure with one *Ar-BIAN* ligand and two chloride atoms coordinated to Hg(II) ion. The larger ionic radius of zinc and cadmium allows for two *Ar-BIAN* ligand molecules to coordinate to the metal ion.

## Experimental

### *Materials and Instrumentation*

All starting materials were purchased from Wako Pure Chemical Industries Ltd., and used without further purification. The bis[*N*-(2,6-diisopropylphenyl)imino]acenaphthene ligand (*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN*) was synthesized from acenaphthenequinone and 2,6-diisopropylaniline as previously reported [6].

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 Series II CHNS/O Analyzer and results were in good accordance with calculated values. Electronic spectra were recorded on a UV-3100PC Shimadzu spectrophotometer using 10 mm quartz cells at room temperature. Powder reflectance spectra were obtained using the same instrument equipped with an integrating sphere and using BaSO<sub>4</sub> as a reference. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer Spectrum 2000 KBr pellets and as Nujol mulls in the 4000–370 cm<sup>-1</sup> spectral range. <sup>1</sup>H and <sup>13</sup>C NMR measurements at room temperature were run on a JEOL JNM LA 300 WB spectrometer at 400 (100) MHz, using a 5 mm probe head in CDCl<sub>3</sub>. Chemical shifts are given in ppm relative to internal *TMS* (tetramethylsilane).

### *X-Ray Data Collection and Structure Refinement of [Hg(*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN*)Cl<sub>2</sub>]*

Crystallographic data and conditions used for the data collection refinement of [Hg(*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN*)Cl<sub>2</sub>] are summarized in Table 3. A prismatic crystal of 0.5 × 0.4 × 0.3 mm was mounted on a Rigaku AFC7R diffractometer using graphite monochromator Cu-Kα radiation at 293 K. Cell constants and orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 20 reflections in the range 3.83 < θ < 68.00°. The ω – 2θ scan mode with a maximum 2θ value being 136° was used to collect intensity data. A total 6741 reflections were collected, of which 6251 had *I* > 2σ(*I*) with 371 parameters. The structure was solved by direct methods SHELXS-86 [18] and refined on *F*<sup>2</sup> using SHELXS-93 [19]. The non-hydrogen atoms were refined anisotropically by full-matrix least squares method. Hydrogen atoms were included, but their positions were not refined. Crystallographic data of [Hg(*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN*)Cl<sub>2</sub>] have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk]. Copies of the data can be obtained free of charge on quoting CCDC 215023.

### *Synthesis of Complexes*

#### *[Hg(*o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN*)Cl<sub>2</sub>] (1, C<sub>36</sub>H<sub>40</sub>Cl<sub>2</sub>HgN<sub>2</sub>)*

A solution of *o,o'*-*iPr*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-*BIAN* (0.35 g, 0.7 mmol) in 25 ml of acetic acid was added to HgCl<sub>2</sub> (0.19 g, 0.7 mmol), dissolved in 25 ml of acetic acid. After 2 h stirring at room temperature the orange product was filtered off, washed with hexane and air-dried. Crystals suitable for X-ray measurements were obtained by recrystallization from hot hexane solution. Yield: 0.45 g (83%); <sup>1</sup>H NMR: δ = 0.91 (d, H23), 1.29 (d, H24), 3.14 (sept, H22), 6.64 (d, H2), 7.33 (s, H15, H16, H17), 7.42 (pst, H3), 7.96 (d, H4); <sup>13</sup>C NMR spectrum was not recorded due to low solubility.

**Table 3.** Crystallographic data and structure refinement for  $[\text{Hg}(o,o'-i\text{Pr}_2\text{C}_6\text{H}_3\text{-BIAN})\text{Cl}_2]$ 

<i>Crystal data</i>	
Empirical formula	$\text{C}_{36}\text{H}_{40}\text{Cl}_2\text{HgN}_2$
Formula weight	772.22
Crystal system	Monoclinic
Space group	$P21/n$
$a$ [Å]	13.494(4)
$b$ [Å]	22.252(4)
$c$ [Å]	11.440(4)
$\alpha, \gamma$ [°]	90.00
$\beta$ [°]	91.10 (3)
$V$ [Å <sup>3</sup> ]	3434 (2)
$Z$	4
Crystal dimensions (mm)	$0.5 \times 0.4 \times 0.3$
$D_{\text{calcd.}}$ [g cm <sup>-3</sup> ]	1.49
$F(000)$	1536
$\mu$ [mm <sup>-1</sup> ]	5.037
<i>Data collection</i>	
Temperature [K]	293(2)
$\theta$ range [°]	3.83–68.00
Radiation	$\text{Cu-K}\alpha$ (Mon), 1.54178 Å
Scan mode	$\omega - 2\theta$
Index ranges	$-16 \leq h \leq 16; 0 \leq k \leq 26; -13 \leq l \leq 1$
Reflections collected	6741
Independent reflections	6263 [ $R(\text{int}) = 0.0874$ ]
<i>Refinement</i>	
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	6251/0/371
Goodness-of-fit on $F^2$	1.180
Final $R$ indices [ $I > 2.00\sigma(I)$ ]	$R_1 = 0.0742, wR_2 = 0.2040$
$R$ indices (all data)	$R_1 = 0.0803, wR_2 = 0.2180$
Extinction coefficient	0.0032(2)
Largest diff. peak and hole	4.036 and $-3.152 \text{ e } \text{Å}^{-3}$

$[\text{Zn}(o,o'-i\text{Pr}_2\text{C}_6\text{H}_3\text{-BIAN})_2](\text{ClO}_4)_2$  (**2**,  $\text{C}_{72}\text{H}_{80}\text{Cl}_2\text{N}_4\text{O}_8\text{Zn}$ )

Both (0.186 g, 0.5 mmol) of  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and (0.5 g, 1.0 mmol) of  $o,o'-i\text{Pr}_2\text{C}_6\text{H}_3\text{-BIAN}$  were mixed and 20 ml of acetic acid was added. After 3 h stirring at room temperature, the red product was filtered, washed with diluted acetic acid followed by hexane and dried in vacuo. Yield 0.53 g (84%);  $^1\text{H}$  NMR:  $\delta = 1.02$  (d, H23), 1.27 (d, H24), 2.95 (sept, H22), 6.91 (d, H2), 7.38 (s, H15, H16, H17), 7.40 (s, H27, H28, H29), 7.48 (pst, H3), 7.63 (pst, H7), 8.32 (d, H4);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 23.3$  (C23), 23.0 (C24), 29.2 (C22), 124.4 (C15, C17), 124.8 (C2), 128.7 (C3), 129.3 (C4), 131.0 (C5), 134.2 (C14, C18), 138.8 (C10), 162.6 (C11).

$[\text{Cd}(o,o'-i\text{Pr}_2\text{C}_6\text{H}_3\text{-BIAN})_2](\text{ClO}_4)_2$  (**3**,  $\text{C}_{72}\text{H}_{80}\text{CdCl}_2\text{N}_4\text{O}_8$ )

$\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.21 g, 0.5 mmol) and  $o,o'-i\text{Pr}_2\text{C}_6\text{H}_3\text{-BIAN}$  (0.5 g, 1.0 mmol) were mixed and 20 ml of acetic acid were added. After 3 h stirring at room temperature, the red product was filtered off, washed with diluted acetic acid followed by hexane, and dried in vacuo. Yield 0.6 g (91%);  $^1\text{H}$  NMR:

$\delta = 1.02$  (d, H23), 1.27 (d, H24), 2.95 (sept, H22), 6.91 (d, H2), 7.38 (s, H15, H16, H17), 7.40 (s, H27, H28, H29), 7.48 (pst, H3), 7.63 (pst, H7), 8.32 (d, H4);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 23.3$  (C23), 23.0 (C24), 29.2 (C22), 124.4 (C15, C17), 124.8 (C2), 128.7 (C3), 129.3 (C4), 131.0 (C5), 134.2 (C14, C18), 138.8 (C10), 162.6 (C11).

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