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Polymethoxyphenyl-Substituted [2-(5-Chloro-2-hydroxy-4-methylphenyl)-2-phenylvinyl]phosphine Oxides: Synthesis and Complexation with Eu(TTA)$_3$

R. R. Zairov, D. A. Tatarinov, N. A. Shamsutdinova, A. R. Mustafina, I. Kh. Rizvanov, V. V. Syakaev, V. F. Mironov, and A. I. Konovalov

Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences,
ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia
e-mail: rustem@iopc.ru

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Abstract—New di- and trimethoxyphenyl-substituted phosphorus-containing ligands, (*Z*)-[2-(5-chloro-2-hydroxy-4-methylphenyl)-2-phenylvinyl]bis(3,4-di- and 3,4,5-trimethoxyphenyl)phosphine oxides, have been synthesized, and their adducts with europium(III) 2-thenoyltrifluoroacetonate have been obtained. High luminescence intensity of the synthesized complexes suggests prospects in using them for the design of various materials possessing unique photophysical properties.

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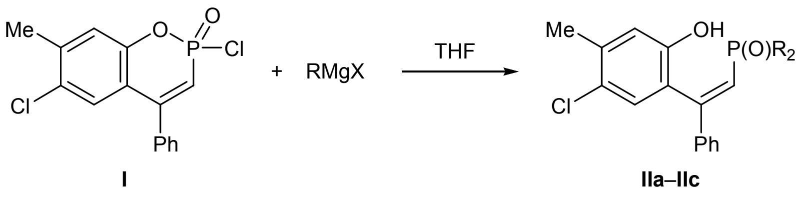
The synthesis of new ligands and their coordination compounds with lanthanide ions, which exhibit efficient luminescence, constitutes a topical problem in modern chemistry [1–3]. For instance, β-diketonate complexes of lanthanides are known as components of luminescent materials [4–6]. In this connection, europium(III) 2-thenoyltrifluoroacetonate Eu(TTA)$_3$ attracts much interest due to its unique photophysical properties which in turn may be improved via formation of ternary complexes with other ligands. Studies on mixed-ligand europium(III) complexes based on europium β-diketonates, including Eu(TTA)$_3$, have been reported in many publications [7–9]. Introduction of an additional ligand possessing some chromophoric properties into the coordination sphere of Eu(III) ion leads to luminescence sensitization [8, 9]. We previously described the synthesis of a new ternary complex of Eu(TTA)$_3$ with (*Z*)-2-(5-chloro-2-hydroxyphenyl)-2-phenylethenyl)bis(2-methoxyphenyl)phosphine oxide (**IIa**), which showed strong luminescence at λ 612 nm ($^5D_0 \rightarrow {}^7F_2$) [10]. It was found that both β-diketonate and phosphine oxide ligands exert an antenna effect on the luminescence of europium(III); as a result, the luminescence intensity of the ternary complex considerably exceeded the luminescence intensity of Eu(TTA)$_3$. Phosphine oxide **IIa** ensured more efficient luminescence sensitization of Eu(III) complexes, as compared to its analogs with methyl and 2-methylphenyl substituents on the phosphorus atom. Therefore, a positive effect of electron-donor methoxy group in the aromatic ring on the phosphorus atom was inferred [10]. Methoxy group is a strong electron donor toward benzene ring, and introduction of two or three methoxy group is expected to enhance the donor power of the aromatic fragment and hence increase the basicity of the phosphoryl group. Taking the above stated

Scheme 1.



R = 2-MeOC$_6$H$_4$ (**a**), 3,4-(MeO)$_2$C$_6$H$_3$ (**b**), 3,4,5-(MeO)$_3$C$_6$H$_2$ (**c**).

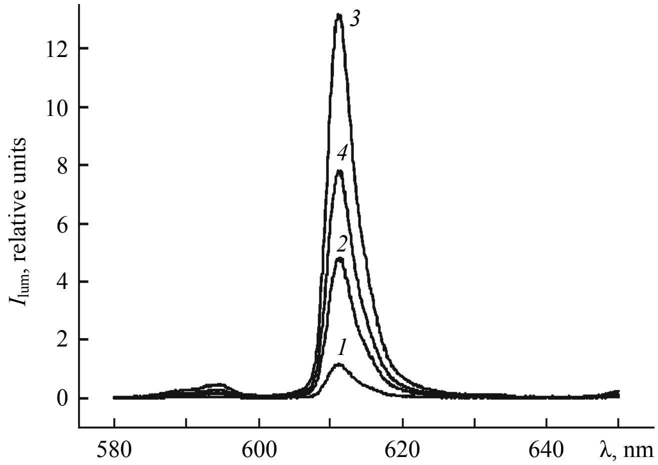


Fig. 1. Emission spectra of (*1*) Eu(TTA)$_3$ ($c = 2.5 \times 10^{-5}$ M) and its 1 : 1 adducts with phosphine oxides (*2*) **IIa**, (*3*) **IIb**, and (*4*) **IIc** in acetonitrile.

into account, it seems reasonable to synthesize new di- and trimethoxyphenyl-substituted phosphine ligands and their complexes with europium(III) 2-thenoyltrifluoroacetonate.

With a view to get a deeper insight into the relations between the structure of phosphorus-containing ligand, peculiar features of its complexation with Eu(TTA)$_3$, and photoluminescence intensity of the resulting mixed-ligand complexes we have synthesized both previously described phosphine oxide **IIa** [10] and new (*Z*)-diaryl[2-(5-chloro-2-hydroxy-4-methylphenyl)-2-phenylethenyl]phosphine oxides **IIb** and **IIc**. The reaction of substituted 1,2-benzoxaphosphinine **I** with organomagnesium compounds derived from 3,4-dimethoxy- and 3,4,5-trimethoxyphenyl bromides was accompanied by a weak exothermic effect, and the products were the corresponding phosphine oxides **IIb** and **IIc** (yield 70–80%; Scheme 1). The isolation of compounds **II** by recrystallization from diethyl ether or acetone took a long time (up to several days).

The structure of phosphine oxides **II** was determined on the basis of their spectral data. In the ^{1}H NMR spectra of **II**, the signal from the methyl group in the hydroxyphenyl substituent appeared in a strong field (δ ~2 ppm), while methoxy protons resonated in a weaker field (δ ~4 ppm). Phosphine oxide **IIc** displayed two signals from the three methoxy groups with an intensity ratio of 2 : 1. The most upfield signals in the aromatic region were those belonging to protons in the *ortho* position to the phenolic hydroxy group (δ ~6.0–6.5 ppm). The proton

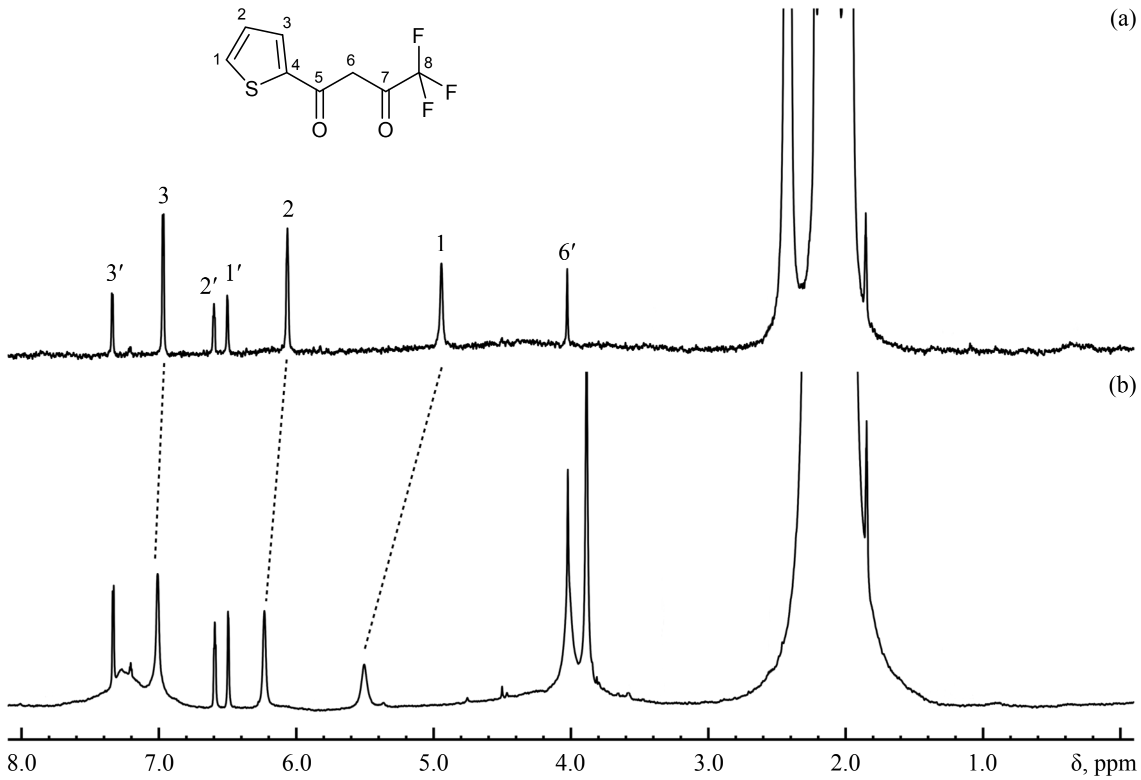


Fig. 2. ^{1}H NMR spectrum of Eu(TTA)$_3$ (1 mM, CD$_3$CN, 600 MHz, 303 K) (a) before and (b) after addition of an equimolar amount of phosphine oxide **IIb**. Primed locants refer to the free ligand.

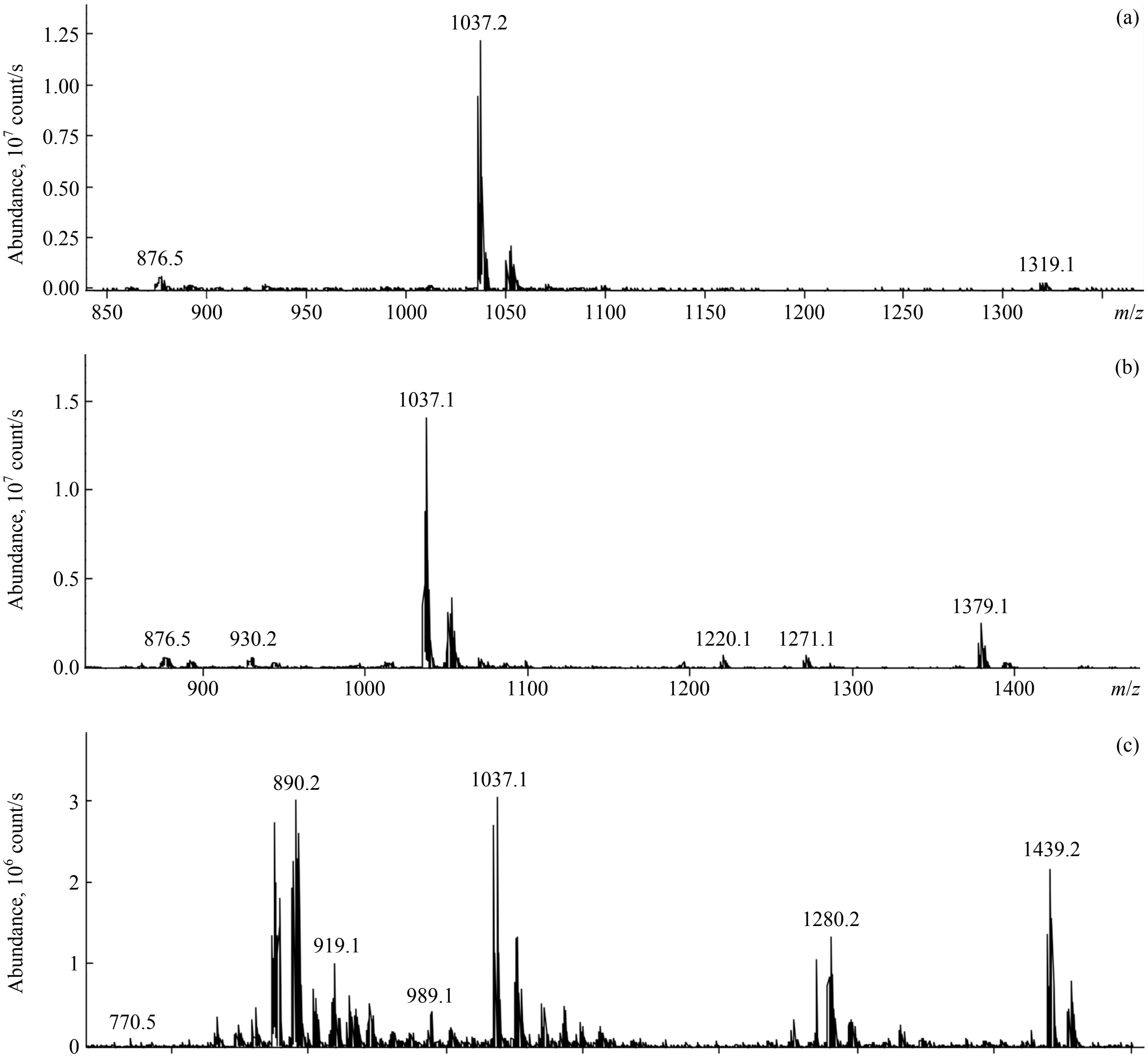


Fig. 3. ESI mass spectra of Eu(TTA)$_3$ complexes with phosphine oxides (a) **IIa**, (b) **IIb**, and (c) **IIc** (propan-2-ol, c = 40 μg/mL).

located in the *ortho* position with respect to the phosphorus atom and methoxy group in **IIb** gave rise to a doublet of doublets at δ 6.86 ppm with the coupling constants $^3J_{PH}$ = 7.8 and $^4J_{HH}$ = 3.0 Hz.

The complexation of Eu(TTA)$_3$ with methoxyphenylphosphine oxides **IIa**–**IIc** was studied in acetonitrile and isopropyl alcohol. These solvents were selected with account taken of the solubility of the initial components and resulting complexes. Addition of phosphine oxides **IIa**–**IIc** to a solution of Eu(TTA)$_3$ increased the luminescence intensity, indicating formation of the corresponding mixed-ligand complexes.

As follows from Fig. 1, the sensitizing effect of phosphine oxide ligands in acetonitrile solution increases in going from monomethoxy- to dimethoxyphenyl-substituted derivatives. Surprisingly, the emission intensity of the trimethoxyphenyl-substituted Eu(TTA)$_3$ derivative was lower than that of its monomethoxy analog. A probable reason is partial rupture of conjugation in the phosphine oxide antenna ligand due to steric repulsion of the substituted benzene rings on the phosphorus atom.

Figure 2 shows that the formation of mixed-ligand complex with phosphine oxide **IIb** is accompanied by

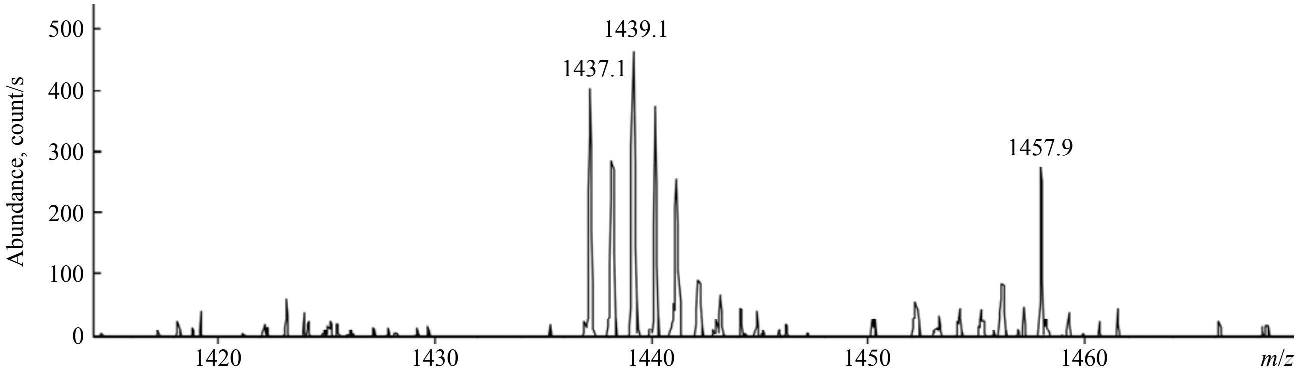


Fig. 4. Isotope distribution in the ESI mass spectrum of Eu(TTA)$_3$·**IIc** (isopropyl alcohol, c = 40 μg/mL); m/z (I_{rel}, %): 1439.05 (100), 1437.05 (75.3), 1440.05 (70.4), 1438.05 (47.2), 1441.04 (41.3), 1439.04 (34.3), 1442.05 (27.4), 1441.05 (27.3), 1443.05 (9.2), 1440.04 (7.0), 1443.04 (5.0), 1442.06 (3.4), 1442.04 (3.2), 1440.06 (2.9), 1444.04 (2.7), 1444.05 (2.5), 1438.04 (1.8), 1443.06 (1.2), 1441.06 (1.1), 1445.05 (1.0).

a downfield shift of proton signals of TTA coordinated to Eu(III), whereas signals from the 1′-H–6′-H protons of the free ligand do not change their position. Broadening of signals of the aromatic protons of phosphine oxide **IIb** reflects the effect of paramagnetic europium(III) ion, which may also be regarded as an evidence of the formation of mixed-ligand complex.

The mass spectra of the complexes (Figs. 3, 4) are in agreement with the luminescence spectroscopy and ^{1}H NMR data. All the examined compounds displayed $[M - \mathrm{H}]^-$ ions (negative ion detection mode) with m/z values of 1319.1, 1379.1, and 1439.1 for Eu(TTA)$_3$·**IIa**, Eu(TTA)$_3$·**IIb**, and Eu(TTA)$_3$·**IIc**, respectively. The ion peak intensity grows in the series **IIa** < **IIb** < **IIc**, which may be due to stabilization of the corresponding complexes. In addition, the mass spectra of all complexes contained a ion peak with m/z 1037.2, which originates from the negative [Eu(TTA)$_4$]$^-$ ion. In all cases, the experimental isotope peak distribution was identical to the theoretical one (hereinafter, peaks with a relative intensity lower than 10% are omitted), m/z (I_{rel}, %): Eu(TTA)$_3$·**IIa**: 1319.1 (100), 1317.1 (65.5), 1320.1 (54.6), 1318.1 (54.6), 1321.1 (51.0), 1322.1 (25.5); Eu(TTA)$_3$·**IIb**: 1379.1 (100), 1377.2 (63), 1380.1 (61.9), 1381.1 (59.5), 1378.1 (40.2), 1382.1 (28.4), 1383.1 (12.6); Eu(TTA)$_3$·**IIb**: 1439.2 (100), 1437.2 (67.6), 1441.1 (63.6), 1440.2 (59.4), 1438.2 (36.4), 1442.1 (31.8), 1443.1 (13.5). Europium occurs as two abundant isotopes with atomic weights of 152 and 154; therefore, europium-containing ion peaks are easily interpretable.

EXPERIMENTAL

The ^{1}H and ^{31}P–{^{1}H} NMR spectra of phosphine oxides **II** were recorded on a Bruker Avance-400 spectrometer at 400 and 162.0 MHz, respectively, using CDCl$_3$ as solvent and reference (for ^{1}H); the ^{31}P chemical shifts were determined relative to H$_3$PO$_4$ as external reference. The ^{1}H NMR spectra of the Eu(TTA)$_3$ complexes with phosphine oxides **II** were measured at 303 K on a Bruker Avance-600 instrument from solutions in CD$_3$CN; the chemical shifts were determined relative to the residual proton signal of the solvent. The IR spectra were obtained on a Bruker Vector-22 spectrometer from samples dispersed in mineral oil or films placed between KBr plates. The mass spectra (electrospray ionization, ESI) were recorded on a Bruker Daltonics AmazonX mass spectrometer with positive and negative ion detection in the a.m.u. range from 500 to 1500 (capillary voltage ±4500 V; nebulizer gas nitrogen, 220°C, flow rate 10 L/min); samples were introduced as solutions in isopropyl alcohol at a concentration c of 40 μg/mL; the data were processed using DataAnalysis 4.0 program (Bruker).

Diaryl[2-(5-chloro-2-hydroxy-4-methylphenyl)-2-phenylethenyl]phosphine oxides IIa–IIc were synthesized according to a modified procedure [11, 12]. A solution of 3 mmol of 2,6-dichloro-7-methyl-4-phenyl-2H-1,2λ^5-benzoxaphosphinine 2-oxide (**I**) in 4 mL of benzene was added dropwise to the Grignard reagent prepared from 0.192 g (8 mmol) of magnesium turnings and 8 mmol of the corresponding halobenzene in 10 mL of THF. The mixture was heated for 0.5 h under reflux and evaporated under reduced pressure on a rotary evaporator, and the residue was cooled to room temperature, treated with water and 4 mL of 20% H$_2$SO$_4$, and extracted with methylene chloride. The organic layer was separated and evaporated on a rotary evaporator, the residue was washed with diethyl ether, and the white precipitate was filtered off and dried at 100°C under reduced pressure (12 mm).

(*Z*)-[2-(5-Chloro-2-hydroxy-4-methylphenyl)-2-phenylvinyl]bis(2-methoxyphenyl)phosphine oxide (IIa). Yield 85%. The properties of the product were consistent with those reported in [10].

(*Z*)-[2-(5-Chloro-2-hydroxy-4-methylphenyl)-2-phenylvinyl]bis(3,4-dimethoxyphenyl)phosphine oxide (IIb). Yield 70%, mp 207°C. IR spectrum, ν, cm^{-1}: 3056, 2924, 2854, 2732, 2635, 2027, 1901, 1658, 1590, 1561, 1511, 1463, 1401, 1378, 1326, 1260, 1237, 1179, 1131, 1111, 1024, 923, 886, 805, 765, 751, 718, 695, 662, 617, 534, 479, 447. ^{1}H NMR spectrum, δ, ppm: 2.21 s (3H, CH_3), 3.81 s (6H, OCH_3), 3.89 s (6H, OCH_3), 6.31 s (1H, 8-H), 6.86 d.d (2H, 14-H, $^3J_{PH}$ = 7.8, $^4J_{HH}$ = 3.0 Hz), 6.92 s (1H, 15-H), 6.99 d (1H, 3-H $^3J_{PH}$ = 19.8 Hz), 7.18 m (4H, 5-H), 7.31 br.m (5H, 14-H). ^{31}P–{^{1}H} NMR spectrum: δ_P 25.4 ppm. Found, %: C 65.87; H 5.33; P 5.44. $C_{31}H_{30}ClO_6P$. Calculated, %: C 65.90; H 5.35; P 5.48.

(*Z*)-[2-(5-Chloro-2-hydroxy-4-methylphenyl)-2-phenylvinyl]bis(3,4,5-trimethoxyphenyl)phosphine oxide (IIc). Yield 68%, mp 124–127°C. IR spectrum, ν, cm^{-1}: 2924, 2854, 2723, 2617, 2229, 2155, 1954, 1581, 1498, 1459, 1404, 1311, 1285, 1241, 1124, 1035, 1003, 925, 888, 807, 764, 695, 651, 626, 612, 554, 493. ^{1}H NMR spectrum, δ, ppm: 2.23 s (3H, CH_3), 3.83 s (12H, *m*-OCH_3), 3.89 s (6H, *p*-OCH_3), 6.45 s (1H, 8-H), 6.89 d (4H, 14-H, 18-H, $^3J_{PH}$ = 14.3 Hz), 6.91 s (1H, 5-H), 6.97 d (1H, PCH, $^2J_{PH}$ = 20.0 Hz), 7.33 m (5H, 10-H, 11-H, 12-H), 8.78 br.s (1H, OH). ^{31}P–{^{1}H} NMR spectrum: δ_P 23.5 ppm. Found, %: C 63.37; H 5.43; P 4.99. $C_{33}H_{34}ClO_8P$. Calculated, %: C 63.41; H 5.48; P 4.96.

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