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Synthesis and solution properties of new metal-free and metallo-phthalocyanines containing four bis(indol-3-yl)methane groups

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ABSTRACT

Metallo-phthalocyanines bearing four bis(indol-3-yl)methane groups were successfully prepared by reaction of the corresponding phthalonitriles with anhydrous metal salts [Zn(CH₃COO)₂, NiCl₂ and CoCl₂] in the presence of a catalytic amount of DBU in 2-(dimethylamino)ethanol. The metal-free phthalocyanine was obtained by treating a mixture of the phthalonitrile derivative in similar conditions but in the absence of a metal salt. All of these phthalocyanines are soluble in DMSO, DMF, and pyridine. The products were characterized by IR, NMR, and UV-vis spectroscopy, MALDI–TOF–MS, and thermogravimetric analysis. The aggregation properties of the phthalocyanines were investigated at different concentrations in DMSO. All the phthalocyanines showed monomeric behavior in solution.

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Phthalocyanines (Pcs) are remarkable compounds possessing photophysical,¹ semiconducting,² and photoconducting properties³ due to their 18 π -electron aromatic macrocyclic structure.⁴ For many years, phthalocyanines have been used as dyes.⁵ Recently, Pc complexes have been investigated in diverse fields such as electronic displays,⁶ photocatalysts,⁷ liquid crystals,^{8,9} photovoltaic cells,¹⁰ electrochromic devices,¹¹ semi-conductors,¹² data storage systems,¹³ chemical sensors,¹⁴ gas sensors,¹⁵ solar cells,¹⁶ nonlinear optics,¹⁷ and as photodynamic therapy (PDT) agents.^{18–20}

Another significant aim of research into the chemistry of phthalocyanines is to enhance their solubility in various solvents. Although, many Pcs have low solubility in common organic solvents, their solubility can be improved by the incorporation of substituents, such as long alkyl, alkoxy, alkylsulfanyl, and other bulky groups.^{21–24} Among the substituted phthalocyanines, those bearing a heterocyclic group, have received considerable attention.²⁵ Different heterocyclic phthalocyanines that have been synthesized and studied include those with xanthene,²⁶ L-prolinol,²⁷ imidazole,²⁸ thiophene,²⁹ pyridine,³⁰ triazole,³¹ and other heterocyclic substituents.

Indole and its derivatives are important in organic chemistry and display a variety of physiological and pharmacological properties.³²

The indole scaffold is an important structural motif in medicinal chemistry.³³ Substituted indoles have been referred to as privileged structures since they are capable of binding to many receptors with high affinity.

Therefore, the development of techniques for the synthesis and functionalization of indoles has been a focus of research over the years.³⁴ Bis(indol-3-yl)methanes feature extensively in bioactive metabolites of terrestrial and marine origin.^{35,36} They also exhibit potent antibacterial activity.³⁷

Due to our interest in the synthesis of bis(indol-3-yl)methanes³⁸ and phthalocyanines,²⁶ we report the synthesis and characterization of several metal free and metallo-phthalocyanines bearing four bis(indol-3-yl)methane groups which enabled the molecules to dissolve in a number of organic solvents such as DMF, DMSO, and pyridine (Scheme 1). A combination of these two potentially promising units [phthalocyanine and bis(indol-3yl)methane groups] may improve their organosolubility and biological properties.

Phthalonitrile derivatives **5a–b** were synthesized in two steps. The first involved a nucleophilic aromatic displacement on 4-nitrophthalonitrile **2** with 4-hydroxybenzaldehyde **1** in the presence of anhydrous K_2CO_3 as the base in DMF to give the dicyano compound **3**. Then compound **3** was reacted with 2 equiv of indole **4** in the presence of alum as the catalyst in acetonitrile at room temperature. Compounds **5a** and **5b** were obtained in 94% and 96% yields, respectively.

The metal-free phthalocyanine **6** was obtained by cyclotetramerization of **5a** using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the catalyst. The reaction was carried out in refluxing 2-(dimethylamino)ethanol (DMAE) under a nitrogen atmosphere. The metallo-phthalocyanines **7–12** were prepared by reaction of phthalonitrile derivatives **5a–b** with anhydrous metal salts $[Zn(CH_3COO)_2, NiCl_2 and CoCl_2]$ in the presence of a few drops of



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Scheme 1. Synthesis of the metal-free and metallophthalocyanines 6–12. Reagents and conditions: (i) K₂CO₃, DMF, 24 h, rt; (ii) alum, CH₃CN, 24 h, rt; (iii) DBU, DMAE, N₂, reflux; (iv) Metal salt, DBU, DMAE, N₂, reflux.

DBU in a high-boiling solvent (DMAE) under a nitrogen atmosphere. Generally, phthalocyanine complexes are insoluble in most organic solvents; however the introduction of substituents on the ring increased their solubility. Phthalocyanine complexes **6–12** showed an excellent solubility in DMF, DMSO, and pyridine. They were insoluble in ether, ethyl acetate, dichloromethane, and acetonitrile. IR, ¹H NMR, MALDI–TOF–MS, and UV–vis spectra were consistent with the proposed structures of the compounds. TGA was used to determine the thermal stability of these complexes.

The IR spectrum of 3 clearly indicated the disappearance of the OH band at 3352 cm^{-1} and the NO₂ bands at 1538 cm^{-1} and 1355 cm^{-1} and the appearance of a CN peak at 2237 cm⁻¹. Moreover, the formation of compounds **5a-b** was consistent with disappearance of the C=O band at 1691 cm^{-1} and the appearance of new bands at 3408 and 3379 cm⁻¹ related to the NH groups for 5a and 5b, respectively. After cyclotetramerization of 5a-b, The IR spectra of phthalocyanines 6-12 lacked the CN band, completely. The ¹H NMR spectrum of **5a** exhibited two singlets at δ : 10.87 and 5.91, respectively, for the NH and CH protons. The aromatic protons resonated in the range of δ : 8.07–6.86. The spectrum of **5b** exhibited three singlets at δ : 10.79, 5.97, 2.12, respectively, for NH, CH, and CH₃ protons. The aromatic protons appeared in the range of δ : 8.12–6.72. In the ¹H NMR spectra of **6**, **7**, **9**, **10**, and **11** resonances for the NH groups were observed at δ : 10.82, 10.85, 10.86, 10.80, and 10.76, respectively. Because of the ring current, the inner N–H proton of compound **6** was shifted to high field and it could not be observed.³⁹ After the cyclotetramerization, the aromatic protons were observed as multiplets at δ : 6.85–7.72, 6.86-7.94, 6.92-7.35, 6.72-7.37, and 6.88-7.22 for 6, 7, 9, 10, and **11**, respectively. The aliphatic CH peaks appeared at δ : 5.93, 5.94, 5.87, 5.97, and 5.98 for 6, 7, 9, 10, and 11, respectively. The CH₃ signals were observed as a multiplet at δ : 2.12–2.33 for **10** and at δ : 1.98–2.13 for **11**.

In the electronic spectrum of the metal-free phthalocyanine **6** (Fig. 1) in DMF, the characteristic split Q absorption band was observed with absorptions at $\lambda_{max} = 697$ and 669 nm with a shoulder at 611 nm. These Q band absorptions show the monomeric species with D₂h symmetry and due to the phthalocyanine ring relate to the fully conjugated 18π -electron system.⁴⁰ The presence of a strong absorption band in the near UV region at $\lambda_{max} = 354$ nm also showed the Soret region B band.

The UV–vis spectra of the metallophthalocyanines **7–12** in DMF are shown in Figure 2. The UV–vis absorption spectra of phthalocyanines **6–12** had intense Q absorptions at λ_{max} = 697, 669, 675, 671, 662, 677, 671, and 663 nm, with weaker absorptions at 611, 609, 605, 599, 611, 613, and 605 nm, respectively. These results are typical of metallophthalocyanines with D₄h symmetry. The B



Figure 1. Absorption spectrum of **6** in DMF (C = 3×10^{-5} M).

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Figure 2. Absorption spectra of metallophthalocyanines 7–12 in DMF (C = 3 \times 10 $^{-5}$ M).

Table 1 Absorption spectral data for phthalocyanines **6–12** in DMF (C = 3×10^{-5} M)

Pcs	$\lambda_{\max}/nm \ (\log \varepsilon)$
6	697(4.17), 669(4.21), 611(3.80), 333(4.34), 275(4.72)
8	675(4.66), 609(4.02), 354(4.36), 277(4.66) 671(4.47), 605(4.02), 278(4.77)
9	662(3.53), 599(4.02), 323(4.45), 275(4.68)
10	677(4.36), 611(3.80), 348(4.30), 271(4.60)
11	671(4.31), 613(3.77), 331(4.30), 272(4.75)
12	656(4.67), 591(4.00), 321(4.52), 272(4.74)

band absorptions of compound **7**, **8**, **9**, **10**, **11**, and **12** were observed at $\lambda_{max} = 275$, 333, 277, 354, 278, 275, 323, 271, 348, 272, 331, 279 nm, respectively (Table 1). The Q band was attributed to the π - π * transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The B band in the UV region was related to the transitions from the deeper π levels to the LUMO.⁴¹

In this study, the aggregation behavior of the phthalocyanines **6–12** was investigated in DMSO at different concentrations. All the phthalocyanines did not show aggregation in this solvent. The aggregation behavior of **10** in DMSO at different concentrations is shown in Figure 3. As the concentration was increased, the intensity of absorption of the Q band also increased and there was no new band (normally blue shifted) due to the aggregated species. So, these complexes exhibited a monomeric form as deduced from the absorption spectra in different concentrations.

The MALDI-TOF-MS measurement for compound **10** gave the characteristic molecular ion peak at m/z: 2035.1 [M]⁺ confirming the proposed structure (Fig. 4).

The thermal properties of all the metal-free phthalocyanines and metallo-phthalocyanines were analyzed by thermal gravimetric analysis (TGA) in the temperature range 30–1000 °C under a nitrogen atmosphere with a heating rate of 10 °C/min. The initial weight loss up to 190 °C was related to the residual solvent which is typical of a TGA heating run. The complexes **6**, **7**, **8**, **11** had two degradation steps and complexes **10** and **12** had three degradation steps, while complex **9** had four degradation steps. The initial decomposition temperatures of the compounds are in the order: **12** > **10** > **6** > **7** > **8** > **11** > **9**. No obvious correlation was observed between the transition metal ions in the phthalocyanine complexes and the initial decomposition temperature (Table 2).

In conclusion, we have synthesized and characterized new metal-free and metallophthalocyanines **6–12** containing four bis(indol-3-yl)methane groups.⁴² All of these phthalocyanines are soluble in DMSO, DMF, and pyridine and did not show aggregation in DMSO. The Pcs reported in this work can be considered as

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Thermal analysis data for 6-12	
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Pcs	Temp of dec (°C)	Mass loss %	Probable %	Nature of probable fragment lost
	uce (c)	found	calcd	
6	200-496	37.85	37.44	6C ₈ H ₆ N
	496-995	38.96	39.13	4C ₇ H ₅ O, C ₆ H ₃ , C ₇ H ₁₀ O
7	197-430	23.71	24.12	$4C_8H_6N$
	430-976	69.17	69.24	C ₈ H ₃ N ₃ , C ₆ H ₃ , 2C ₈ H ₃ N ₃ 4C ₇ H ₅ O,
				4C ₈ H ₆ N,
8	195-420	24.15	24.20	$4C_8H_6N$
	420-910	68.71	69.46	C ₈ H ₃ N ₃ , C ₆ H ₃ , 2C ₈ H ₃ N ₃ 4C ₇ H ₅ O,
				$4C_8H_6N$,
9	190-384	18.18	18.15	3C ₈ H ₇ N
	384-502	12.41	12.10	2C ₈ H ₇ N
	502-582	6.12	6.05	C ₈ H ₇ N
	582-915	32.41	30.60	4C ₇ H ₅ O, 2C ₈ H ₇ N
10	210-432	22.87	22.94	8CH ₃ , 3C ₈ H ₇ N
	432-586	21.62	21.72	2C ₇ H ₅ O, 2C ₈ H ₇ N
	586-905	45.35	45.42	C ₈ H ₃ N ₂ C ₈ H ₃ N, C ₈ H ₃ N ₃ , C ₇ H ₆ ,
				C ₇ H ₅ O, 3C ₈ H ₇ N
11	192-450	28.88	28.68	4C ₈ H ₇ N, 8CH ₃
	450-975	50.20	50.32	C ₈ H ₃ N ₃ , 4C ₇ H ₅ O 4C ₈ H ₇ N,
12	230-471	28.31	28.63	4C ₈ H ₇ N, 8CH ₃
	471-613	22.56	22.68	4C ₈ H ₇ N
	613-921	43.69	43.89	C ₈ H ₃ N, C ₆ H ₃ 4C ₇ H ₅ O, 2C ₈ H ₃ N ₃



Figure 3. Aggregation behavior of **10** in DMSO at different concentrations: 6×10^{-5} M (A), 5×10^{-5} M (B), 4×10^{-5} M (C), 3×10^{-5} M (D).



Figure 4. MALDI-TOF-MS spectrum of 10.

efficient candidates for solution studies requiring the monomeric form of such materials as in the case of the photosensitizers used in photodynamic therapy.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/i.tetlet.2012.07.046.

References and notes

- 1. (a) Huang, S.; Dai, L.; Mau, A. W. H. J. Phys. Chem. B 1999, 103, 4223-4227; (b) Hanack, M.; Lang, M. Adv. Mater. 1994, 6, 819-833; (c) Matlaba, P.; Nyokong, T. Polyhedron 2002, 21, 2463-2472.
- 2. Kumar, T. M. M.; Ahcar, B. N. J. Organomet. Chem. 2006, 691, 331-336.
- Viricelle, J. P.; Pauly, A.; Mazet, L.; Bouvet, J. M.; Varenne, C.; Pijolat, C. Mater. Sci. Eng. C. 2006, 26, 186-195.
- Leznoff, C. C.; Lever, A. B. P. In Phthalocyanine: Properties and Applications; VCH: New York, 1993; Vol. 3,
- Moser, F.; Thomas, H. A. L. Phthalocyanine Compounds; Reinhold Publ: New York, 1963.
- Li, D.; Le, Y.; Hou, X. Y.; Chen, J. F.; Shen, Z. G. Synth. Met. 2011, 161, 1270-1275.
- Wohrle, D.; Suvorova, O.; Bartels, R. O.; Lapok, L.; Baziakina, N.; Makarov, S.; Slodek, A. J. Porphyr. Phthalocya. 2004, 8, 1020-1041.
- Torre, G.; Bottari, G.; Hahn, U.; Torres, T. Struct. Bond. **2010**, 135, 1–44.
- Nyokong, T. Struct. Bond. 2010, 135, 45-87.
- (a) Kikuchi, E.; Kitada, S.; Ohno, A.; Aramaki, S.; Maenosono, S. Appl. Phys. Lett. 10. 2008, 92, 173307-173309; (b) Yamada, H.; Kamio, N.; Ohishi, A.; Kawano, M.; Okujima, T.; Ono, N. J. Porphyr. Phthalocya. 2007, 11, 383-389.
- de la Torre, G.; Claessens, C. G.; Torres, T. Chem. Commun. 2007, 2000-2015. 11
- Zhang, Y.; Cai, X.; Bian, Y.; Jiang, J. Struct. Bond. 2010, 135, 275-322. 12
- Shuguang, B.; Xianggao, L.; Lei, S.; Jianfeng, C.; Mater, J. Sci. Technol. 2006, 22, 13. 533-535
- Zhang, Y. J.; Hu, W. P. Sci. China Ser. B 2009, 52, 751-754. 14.
- Sizun, T.; Bouvet, M.; Chen, Y.; Suisse, J.; Barochi, G.; Rossignol, J. Sensor. Actuat. 15. B. -Chem. 2011, 159, 163-170.
- Yang, F.; Forrest, S. R. J. Am. Chem. Soc. 2008, 2, 1022-1032. 16
- Liu, Y.; OFlaherty, S. M.; Chen, Y.; Araki, Y.; Bai, J.; Doyle, J.; Blau, W. J.; Ito, O. 17. Dves Pigments 2007 75 88-92
- Herlambang, S.; Kumagai, M.; Nomoto, T.; Horie, S.; Fukushima, S.; Oba, M.; 18. Miyazaki, K.; Morimoto, Y.; Nishiyama, N.; Kataoka, K. J. Control. Release. 2011, 155, 449-457.
- Master, A. M.; Rodriguez, M. E.; Kenney, M. E.; Oleinick, N. L.; Gupta, A. S. J. 19. Pharm. Sci. 2010, 99, 2386–2398.
- 20. Bonnet, R.; Martinez, G. Tetrahedron 2001, 57, 9513-9547.
- Banfi, S.; Carous, E.; Buccafurni, L. J. Organomet. Chem. 2007, 692, 1269-1276. 21.
- 22. Dincer, H. A.; Koca, A.; Gul, A.; Kocak, M. B. Dyes Pigments 2008, 76, 825-831.
- Sessler, J. L.; Jayawickramarajah, J.; Gouloumis, A.; Pantos, G. D.; Torres, T.; Guldi, D. M. *Tetrahedron* **2006**, *62*, 2123–2131. 23.
- Cammidge, A. N.; Berber, G.; Chambrier, I.; Hough, P. W.; Cook, M. J. 24. Tetrahedron 2005, 61, 4067-4074.
- Hamuryudan, E.; Merey, S.; Bayır, Z. A. Dyes Pigments **2003**, *59*, 263. Karimi, A. R.; Bayat, F. Tetrahedron Lett. **2012**, *53*, 123. 25
- 26.
- Karaca, H.; Sezer, S.; Tanyeli, C. Dyes Pigments 2011, 90, 100. 27
- 28. Yabaş, E.; Sülü, M.; Saydam, S.; Dumludağ, F.; Salih, B.; Bekaroğlu, Ö. Inorg. Chim. Acta 2011, 365, 340.
- Knwby, D. M.; Swager, T. M. Chem. Mater. 1997, 9, 535. 29
- Booysen, I.; Matemadombo, F.; Durmus, M.; Nyokong, T. Dyes Pigments 2011, 30. 89, 111.

- 31. Bekircan, O.; Bıyıklıoğlu, Z.; Acar, I.; Bektas, H.; Kantekin, H. J. Organomet. Chem. 2008, 693, 3425
- 32 Tois, J.; Franzen, R.; Koskinen, A. Tetrahedron 2003, 59, 5395-5405.
- 33. Faulkner, D. J. Nat. Prod. Rep. 2001, 18, 1-49.
- (a) Gilchrist, T. L. J. Chem. Soc., Perkin Trans. 1 2001, 2491–2515; (b) Cacchi, S.; 34. Fabrici, G. Chem. Rev. 2005, 105, 2873-2920; (c) Humphrey, G. R.; Kuethe, J. T. Chem. Rev. 2006, 106, 2875–2911.
- 35. (a) Osawa, T.; Namiki, M. Tetrahedron Lett. 1983, 24, 4719-4722; (b) Garbe, T. R.; Kobayashi, M.; Shimizu, N.; Takesue, N.; Ozawa, M.; Yukawa, H. J. Nat. Prod.
 - 2000, 63, 596-598. 36 Morris, S. A.; Anderson, R. J. Tetrahedron 1990, 46, 715-720.
 - Hong, C.; Firestone, G. L.; Bjeldanes, L. F. Biochem. Pharmacol. 2002, 63, 1085-37. 1097
 - 38. Azizian, J.; Mohammadi, A. A.; Karimi, N.; Mohammadizadeh, M. R.; Karimi, A. R. Catal. Commun. 2006, 7, 752-755.
 - 39 Hirsch, A.; Hanack, M. Chem. Ber. 1991, 124, 833-839.
 - Muranaka, A.; Okuda, M.; Kobayashi, N.; Somers, K. J. Am. Chem. Soc. 2004, 126, 40. 4596-4604.
 - Makarov, S. G.; Suvorova, O. N.; Litwinski, C.; Ermilov, E. A.; Roeder, B.; 41. Tsaryova, O.; Duelcks, T.; Woehrle, D. Eur. J. Inorg. Chem. 2007, 4, 546-552.
 - Synthesis of 4-(4-formylphenoxy)phthalonitrile (3): A mixture of 4-42 hydroxybenzaldehyde 1 (0.122 g, 1 mmol), 4-nitrophthalonitrile 2 (0.173 g, 1 mmol), and K₂CO₃ (0.138 g, 1 mmol) was dissolved in 2 mL DMF. The mixture was stirred at room temperature for 24 h. After completion of the reaction, 1 mL acetone and 5 mL water were added to the reaction mixture and the resulting precipitate was separated and washed with 10 mL hot water and 10 mL hot ethanol. Yield: 85%, mp: 154 °C. IR (KBr) (v_{max}, cm⁻¹): 3103, 3078, 3041, 2850, 2760, 2237, 1691, 1589, 1491, 1408, 1311, 1257, 1211, 1157, 1087, 705, 588, 526. Synthesis of 4-(4-(di(1H-indol-3-821. yl)methyl)phenoxy)phthalonitrile (5a): Compound 3 (0.248 g, 1 mmol), indole (0.234 g, 2 mmol) and alum (0.0478 g, 0.1 mmol) were dissolved in 3 mL acetonitrile. The mixture was stirred at room temperature for 24 h. After completion of the reaction, the solid was filtered off and washed with 10 mL hot water and 10 mL hot ethanol. Yield: 94%, mp: 102 °C. IR (KBr) (v_{max} , cm⁻¹): 3408, 3041, 2847, 2231, 1591, 1564, 1485, 1421, 1280, 1249, 1205, 1091, 744. ¹H NMR (400 MHz, DMSO- d_6) δ_{H} : 10.87 (s, 2H, NH), 8.07 (d, J = 6.6 Hz, 1H, H_{arom}), 7.76 (d, J = 2.1 Hz, 1H, H_{arom}), 7.47 (d, J = 6.3 Hz, 2H, H_{arom}), 7.30–7.37 (m, 5H, H_{arom}), 7.03–7.44 (m, 4H, H_{arom}), 6.86–6.90 (m, 4H, H_{arom}), 5.91 (s, CH, 1H). Synthesis of metal-free phthalocyanine (6): A mixture of compound 5a (0.10 g, 0.21 mmol), three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 2-(dimethylamino)ethanol (DMAE) (10 mL) was refluxed at 130 °C under nitrogen atmosphere for 18 h. After cooling to room temperature the mixture was treated with EtOH (2 mL) in order to precipitate the product. The precipitated dark green product was filtered off and washed with 10 mL hot ethanol and 10 mL hot water. Yield: 46%. IR (KBr) (v_{max}, cm⁻¹): 3391, 3275, 1601, 1500, 1456, 1354, 1263, 1230, 1167, 1093, 1012, 742, 279. ¹H NMR (300 MHz, DMSO-d₆) δ: 10.82 (8H, NH), 6.85-7.72 (m, 68H, H_{arom}), 5.93 (CH, 4H). Synthesis of Zinc(II) phthalocyanine (7): A mixture of compound 5a (0.10 g, 0.21 mmol), $Zn(CH_3COO)_2$ (0.013 g, 0.07 mmol), three drops of (DBU), and DMAE (7 mL) was refluxed at 130 °C under nitrogen atmosphere for 18 h. After cooling to room temperature the mixture was treated with EtOH (2 mL) in order to precipitate the product. The precipitated dark green product was filtered off and washed with 10 mL hot ethanol and 10 mL hot water. Yield: 47%. IR (KBr) (v_{max}, cm⁻¹): 3385, 3055, 2928, 2854, 1653, 1601, 1500, 1456, 1338, 1228, 1095, 742. ¹H NMR (300 MHz, DMSO-*d*₆) δ_H: 10.85 (8H, NH), 6.86– 7.94 (m, 68H, H_{arom}), 5.94 (CH, 4H).