Synthesis of cyclopropane-1,1,2,2-tetracarboxylic acid derivatives from aldehydes and CH-acids in the $K_2CO_3/Bu^n_4NPF_6$/toluene heterogeneous system*

*G. V. Kryshtal, G. M. Zhdankina, and S. G. Zlotin**

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 135 5328. E-mail: zlotin@ioc.ac.ru

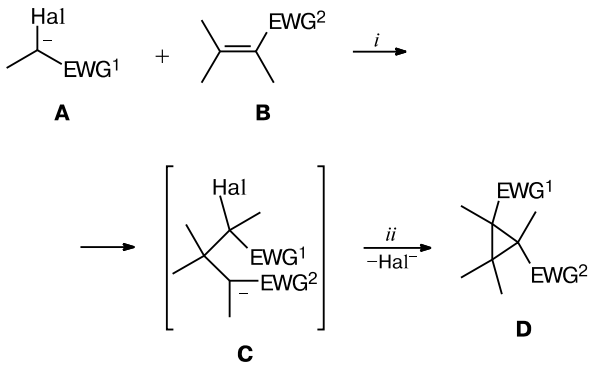
A one-pot method for the synthesis of cyclopropane-1,1,2,2-tetracarboxylic derivatives was developed starting from aldehydes and cyanoacetic and 2-bromomalonic esters under heterogeneous conditions (K_2CO_3/PhMe) in the presence of recoverable phase-transfer catalyst $Bu^n_4NPF_6$.

Key words: cyclopropanation, phase-transfer catalysis, ionic liquids.

Cyclopropanecarboxylic acid derivatives possess biological activities (antibacterial, insecticide, acaricide, fungicide, *etc.*)[1,2] and are used in medicine,[2b,3] and agriculture.[2c,e] In addition, a possibility of modification of functional groups and the presence strained small ring make them important synthons in organic synthesis.[1,4,5] A base-promoted domino reaction between CH-acids containing a halogen atom at the nucleophilic carbon atom and electron-deficient alkenes is a convenient method for their preparation. This reaction, commonly known as the Michael initiated ring closure (MIRC),[6a] includes 1,4-addition of α-halogenated CH-acid anion **A** to alkene **B** and subsequent intramolecular substitution for the halogen atom (bromine or chlorine) in the intermediate **C** with the formation of cyclopropane **D** (see Ref. 6, Scheme 1). Such an approach has been used for the synthesis of cyclopropanes bearing various electron-withdrawing substituents (EWG = CHO, COR, CO_2R, CN, $C(O)NR_2$, NO_2, *etc.*).

The Knoevenagel adducts[7] obtained from aldehydes and malonic, acetoacetic, cyanoacetic, or nitroacetic derivatives are usually used as electrophiles **B**. In some cases, the Knoevenagel reaction and MIRC can be carried out in one vessel as a three-component process involving one carbonyl component and two CH-acids (one of them should bear a halogen atom). Thus, electrolysis of two equivalents of malononitrile (or ethyl cyanoacetate) and a ketone (aldehyde) in ethanolic NaBr in EtOH leads to cyclopropanepolycarboxylic derivatives (in this case, the bromo derivative **A** is generated *in situ* from a CH-acid and NaBr), however, in such a procedure one cannot use a mixture of different CH-acids, which makes the range of its application limited.[8] Recently, cyclopropanecarboxylic derivatives have been successfully obtained by a sequence of the Knoevenagel reaction and MIRC involving two different CH-acids, however this required prolonged heating the components in the presence of piperidine[9] or pyridine.[10]

Scheme 1



i. The Michael reaction. *ii*. Cyclization.

We suggest a new, mild, and efficient method for the three-component synthesis of cyclopropanes under heterogeneous conditions (K_2CO_3—toluene) in the presence of fluorine-containing phase-transfer catalyst (PTC) $Bu^n_4NPF_6$, an analog of ionic liquids. In the literature, there are examples when ionic liquids are used as solvents and acid-base catalysts of the Knoevenagel reaction[11,12] and MIRC,[13] however, they have not been used earlier in these reactions as PTC.

First of all, we studied a K_2CO_3-induced condensation of benzaldehyde (**1a**) with ethyl cyanoacetate (**2**) without PTC and in the presence of tetraalkylammonium or

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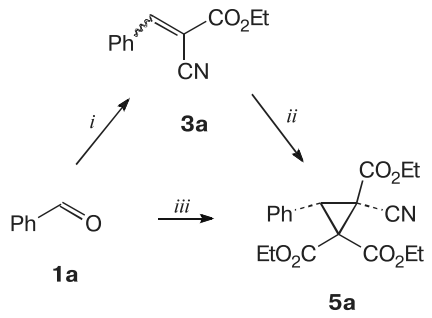
Scheme 2



Reagents, conditions, and yields: *i*. $NCCH_2CO_2Et$ (**2**), K_2CO_3/PTC (5 mol.%), PhMe, 20 °C, 4 h; *ii*. $BrCH(CO_2Et)_2$ (**4**), K_2CO_3/$Bu^n_4NPF_6$ (5 mol.%), PhMe, 20 °C, 4.5 h, the yield was 98%; *iii*. 1) $NCCH_2CO_2Et$ (**2**), 2) $BrCH(CO_2Et)_2$ (**4**), K_2CO_3/$Bu^n_4NPF_6$ (5 mol.%), PhMe, 20 °C, the yield was 94%.

Table 1. Optimization of conditions for the synthesis of **3a** from benzaldehyde (**1a**) and ethyl cyanoacetate (**2**)

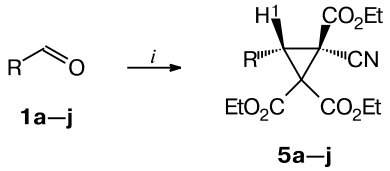
Entry	PTC	Yield (%) (cycle)	
		3a	recovered catalyst
1	—	0	—
2	$BnEt_3NCl$	82	0
3	[bmim]BF_4	86	0
4	$Bu^n_4NBF_4$	97	55
5	$Bu^n_4NPF_6$	97 (1), 98 (2), 98 (3)	96 (1), 95 (2), 95 (3)

1-butyl-3-methylimidazolium salts with the Cl^-, BF_4^-, and PF_6^- anions. The reactions were carried out under comparable conditions (toluene, 20 °C, 4 h) (Scheme 2, Table 1). It turned out that the reaction does not occur in the absence of PTC, however, addition of an ammonium salt (5 mol.%) to the system gives product **3a**, whose yield was the highest (89%) in the case of tetrabutylammonium hexafluorophosphate $Bu^n_4NPF_6$ (see Refs 14 and 15). It is important that this PTC, being poorly soluble in toluene and water, is easy separated from the product and can be used no less than three times with the same efficiency (see Table 1, entry *5*).

We found that in the same heterogeneous system, the Knoevenagel adduct **3a** with diethyl bromomalonate (**4**) gives cyclopropane **5a** in 98% yield, exceeding the yields reported in the literature (62% in the system K_2CO_3/DMF/BTEA-Cl,[16] 82% during electrolysis[17]). The identical conditions allows us to synthesize product **5a** from compounds **1a**, **2**, and **4** excluding the step of isolation of the intermediate **3a**. After the Knoevenagel reaction reached completion, bromomalonate **4** was added to the reactor to furnish **5a** in 94% yield calculated from the introduced aldehyde **1a**.

It turned out that various (aromatic, heteroaromatic, and aliphatic) aldehydes **1a—i**, including prenyl-containing ones **1d—f**, can be involved into the tandem sequence of the Knoevenagel reaction and MIRC under conditions found. The corresponding cyclopropane derivatives were obtained in high yields (Scheme 3, Table 2). Depending on the ratio of components, dialdehyde **1g** forms products

Scheme 3



Reagents and conditions: *i*. 1) $NCCH_2CO_2Et$ (**2**), 2) $BrCH(CO_2Et)_2$ (**4**), K_2CO_3/$Bu^n_4NPF_6$ (5 mol.%), PhMe, 20 °C.

Table 2. One-pot synthesis of cyclopropanetetracarboxylic acid derivatives **5a—j**

Entry	**1**	R	τ/h		**5**	Yield of **5** (%)
			Step 1	Step 2		
1	**a**	Ph	4.0	3	**a**	94
2	**b**	4-$O_2NC_6H_4$	3.0	6	**b**	89[a]
3	**c**	4-$MeOC_6H_4$	30.0[b]	8	**c**	91
4	**d**	Me_2C=CH	2.0	4	**d**	95
5	**e**	Me_2C=CH$(CH_2)_2C(Me)$=CH	2.0	12	**e**	88[a]
6	**f**	Me_2CHCH_2	8.0	12	**f**	85
7	**g**	4-$OCHC_6H_4$	2.0	7	**g**	91[a]
8	**h**	2-Furyl	2.5	5	**h**	94
9	**i**	2-Thienyl	9.0	6	**i**	91
10	**g**	4-$OCHC_6H_4$	10.0	15	**j**[c]	95

[a] The reaction was carried out in the presence of PTC recovered from the preceding experiment.
[b] The first step of the reaction was carried out at 45 °C.
[c] Compound **5j** was obtained at the molar ratio of reagents **1** : **2** : **4** = 1 : 2 : 2.

5g and **5j** containing one or two cyclopropane rings. In this case, efficiency of the reactions do not decrease if they are carried out in the presence of PTC recovered from the preceding experiments (see Table 2, entries *2*, *5*, and *7*).

The NMR data show that the process is stereoselective. A mutual *E*-arrangement of the substituent R and the ester group in the known products[16—19] **5a**,**c** (data for the trimethyl ester are given in Ref. 17) and **5d**,**e** (see Ref. 16) was confirmed by comparison of chemical shifts for the proton of the cyclopropane ring H^1 with the δ values for the known compounds. Thus, the value $\delta_H{}^1 = 3.93$ in the product **5a** agrees with the value $\delta_H{}^1$ for compound *E*-**5a**[17,19] and differs from the corresponding value for isomer *Z*-**5a** (δ 4.01).[19] The new compounds **5b**,**f**—**j**, which were characterized by the IR, ^{1}H and ^{13}C NMR spectral data and microanalytical data, were assigned the structure of *E*-isomers by analogy. Compound **5e** consists of two isomers differing in configuration of the double bond in the isoprenoid group, since commercially available mixture of *E*- and *Z*-citrals 65/35 was used for the synthesis of the starting aldehyde **1e**.

In conclusion, we suggested simple and efficient procedure for the synthesis of cyclopropane-1,1,2,2-tetracarboxylic derivatives from aldehydes and cyanoacetic and 2-bromomalonic esters under heterogeneous conditions (K_2CO_3/PhMe) in the presence of recoverable PTC $Bu^n{}_4NPF_6$.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 and 75.47 MHz, respectively) in $CDCl_3$. IR spectra were recorded on a Specord M-82 spectrometer. Elemental analysis was performed on a Perkin—Elmer 2400 microanalyzer. Reaction progress was monitored by TLC on Silufol plates (eluent: *n*-hexane—EtOAc, 8 : 2, visualization with the UV light and I_2 vapors). Purification of products was performed by column chromatography on silica gel (Acros, 0.060—0.200 mm). Aldehydes **1a**—**i**, ethyl cyanoacetate (**2**), diethyl bromomalonate ester (**4**), catalysts $Bu^n{}_4NBF_4$, [bmim]BF_4, $BnEt_3NCl$, and K_2CO_3 (Acros) were used as purchased. The $Bu^n{}_4NPF_6$ catalyst was synthesized according to the known method.[15]

Optimization of the Knoevenagel reaction conditions. A mixture of compounds **1a** (1.06 g, 1 mmol), **2** (1.13 g, 1 mmol), K_2CO_3 (1.38 g, 1 mmol), and a catalyst (5 mol.%) (see Table 1) in toluene (3.0 mL) was vigorously stirred for 4 h at 20 °C. The reaction mixture was diluted with water (if $Bu^n{}_4NPF_6$ or $Bu^n{}_4NBF_4$ were used, the catalyst was filtered off) and extracted with Et_2O (2×5 mL). The combined organic extract was washed with water (20 mL) and dried with $MgSO_4$, the solvent was evaporated at reduced pressure (40 °C, 40 Torr). A crude product was purified on a column with SiO_2, eluting sequentially with *n*-hexane and its mixture with EtOAc. The yields of **3a** and amount of recovered catalyst ($Bu^n{}_4NPF_6$ was reused in two more reaction cycles) are given in Table 1.

Synthesis of compound 5a from 3a. A solution of **4** (1.2 g, 0.5 mmol) in toluene (2.0 mL) was added to a suspension of **3a** (1.0 g, 0.5 mmol), K_2CO_3 (0.7 g, 0.5 mmol), and $Bu^n{}_4NPF_6$ (0.1 g, 5 mol.%) in toluene (2.0 mL) with vigorous stirring. The reaction mixture was stirred at 20 °C for 4.5 h (TLC monitoring) and diluted with water, the catalyst was filtered off, the filtrate was extracted with Et_2O (2×5 mL). The combined organic extract was washed with water (20 mL) and dried with $MgSO_4$, the solvent was evaporated at reduced pressure (40 °C, 40 Torr). A crude product was purified on a column with SiO_2, eluting sequentially with *n*-hexane and its mixture with EtOAc to obtain **5a** (1.75 g, 98%) as a colorless oil.

Synthesis of compounds 5a—j from 1a—i. A mixture of compounds **1** (0.5 mmol), **2** (0.57 g, 0.5 mmol), K_2CO_3 (0,7 g, 0.5 mmol), and $Bu^n{}_4NPF_6$ (0.1 g, 5 mol.%) in toluene (2.0 mL) was vigorously stirred at the indicated temperature (see Table 2, step *1*) until **1** disappeared (TLC monitoring), after which a solution of **4** (1.2 g, 0.5 mmol) in toluene (2.0 mL) was added, and the stirring was continued at the indicated temperature (see Table 2, steps *2* and *3*, TLC monitoring). Then, the reaction mixture was diluted with water, the catalyst was filtered off, the filtrate was extracted with Et_2O (2×5 mL). The combined organic extract was washed with water (20 mL) and dried with $MgSO_4$, the solvent was evaporated at reduced pressure (40 °C, 40 Torr). A crude product was purified on a column with SiO_2, eluting sequentially with *n*-hexane and the *n*-hexane—EtOAc solvent mixture. The yields of products **5a**—**j** are given in Table 2. Physicochemical properties, the IR spectral data, ^{1}H and ^{13}C NMR spectral data, as well as results of elemental analysis of the newly synthesized compounds **5** are given below.

Triethyl (*E*)-2-cyano-3-phenylcyclopropane-1,1,2-tricarboxylate (5a). A colorless oil, $n_D{}^{20}$ 1.5040. ^{1}H NMR, δ: 1.09, 1.31 and 1.39 (all t, 3 H each, 3 Me, J = 7.0 Hz); 3.93 (s, 1 H, CH); 4.13, 4.26 and 4.34 (all q, 2 H each, 3 OCH_2, J = 7.0 Hz); 7.27—7.40 (m, 5 H, Ph).

Triethyl (*E*)-2-cyano-3-(4-nitrophenyl)cyclopropane-1,1,2-tricarboxylate (5b). A light yellow powder, m.p. 123—124 °C. IR (KBr), ν/cm^{-1}: 1352, 1556 (NO_2); 1755 (C=O); 2249 (CN). ^{1}H NMR, δ: 1.16, 1.32 and 1.41 (all t, 3 H each, 3 Me, J = 7.0 Hz); 3.97 (s, 1 H, CH); 4.18, 4.29 and 4.37 (all q, 2 H each, 3 OCH_2, J = 7.0 Hz); 7.60 (d, 2 H, Ar, J = 8.8 Hz); 8.25 (d, 2 H, Ar, J = 8.8 Hz). ^{13}C NMR, δ: 13.7, 13.9, 14.0, 30.8, 38.1, 47.6, 63.1, 63.4, 64.6, 112.9, 123.9, 129.9, 137.1, 147.9, 162.1, 163.3, 163.7. Found (%): C, 56.62; H, 4.87; N, 6.85. $C_{19}H_{20}N_2O_8$. Calculated (%): C, 56.43; H, 4.99; N, 6.93.

Triethyl (*E*)-2-cyano-3-(4-methoxyphenyl)cyclopropane-1,1,2-tricarboxylate (5c). A white powder, m.p. 74—75 °C. ^{1}H NMR, δ: 1.15, 1.31 and 1.39 (all t, 3 H each, 3 Me, J = 7.0 Hz); 3.80 (s, 3 H, OMe); 3.87 (s, 1 H, CH); 4.17, 4.28 and 4.34 (all q, 2 H each, 3 OCH_2, J = 7.0 Hz); 6.89 (d, 2 H, Ar, J = 8.8 Hz); 7.30 (d, 2 H, Ar, J = 8.8 Hz).

Triethyl (*E*)-2-cyano-3-(2-methylpropenyl)cyclopropane-1,1,2-tricarboxylate (5d). A colorless oil, $n_D{}^{20}$ 1.4745. ^{1}H NMR, δ: 1.25, 1.27 and 1.32 (all t, 3 H each, 3 Me, J = 7.0 Hz); 1.79 and 1.81 (both s, 3 H each, Me_2C); 3.34 (d, 1 H, CH, J = 8.1 Hz); 4.17, 4.25 and 4.27 (all q, 2 H each, 3 OCH_2, J = 7.0 Hz); 5.19 (m, 1 H, CH).

Triethyl (*E*)-2-cyano-3-(2,6-dimethylhepta-1,5-dienyl)cyclopropane-1,1,2-tricarboxylate (5e) (a mixture of *Z*/*E*-isomers 35/65 in the isoprenoid substituent R). A colorless oil, $n_D{}^{20}$ 1.4800. ^{1}H NMR, δ: 1.27, 1.28 and 1.34 (all t, 3 H each, 3 Me,

J = 7.0 Hz); 1.59 and 1.69 (both s, 3 H each, Me_2C); 1.80 (*Z*-isomer) and 1.82 (*E*-isomer) (both s, *Z*/*E* = 35/65, 3 H, C(Me)); 2.10—2.25 (m, 4 H, 2 CH_2); 3.33—3.40 (m, 1 H, CH); 4.22, 4.26 and 4.29 (all q, 2 H each, 3 OCH_2, J = 7.0 Hz); 5.02—5.15 (m, 1 H, CH); 5.22 (d, 1 H, CH, J = 8.1 Hz). ^{13}C NMR, δ: 13.8, 13.9, 14.0 (all $\underline{Me}CH_2O$); 17.4 and 26.3 ($\underline{Me}_2C$); 17.6 and 25.6 (C($\underline{Me}$)); 23.7 (CH_2); 31.3 and 39.5 (CH_2); 33.0, 35.3, 47.5 (all C_{cycle}); 62.6, 62.9, 63.8 (all OCH_2); 112.6 (CN); 123.2 and 123.4 ((Me)C=$\underline{C}$H); 129.8 (Me_2C=$\underline{C}$H); 132.5 ($Me_2\underline{C}$); 146.7 and 146.8 ($\underline{C}$(Me)); 162.7, 163.8, 164.3 (all C=O).

Triethyl (*E*)-2-cyano-3-isobutylcyclopropane-1,1,2-tricarboxylate (5f). A colorless oil, n_D^{20} 1.4550. IR (neat), ν/cm^{-1}: 1748 (C=O), 2256 (CN). ^{1}H NMR, δ: 0.94 and 0.98 (both d, 3 H each, 2 Me, J = 6.6 Hz); 1.23, 1.27 and 1.31 (all t, 3 H each, 3 Me, J = 7.0 Hz); 1.63—1.81 (m, 3 H, CH_2, CH); 2.59 (t, 1 H, CH, J = 7.0 Hz); 4.16, 4.24 and 4.26 (all q, 2 H each, 3 OCH_2, J = 7.0 Hz). ^{13}C NMR, δ: 13.6, 13.7, 13.8, 21.8, 21.9, 27.5, 30.5, 35.0, 38.1, 46.5, 62.3, 62.7, 63.5, 112.8, 163.0, 163.9, 164.2. Found (%): C, 60.24; H, 7.47; N, 4.20. $C_{17}H_{25}NO_6$. Calculated (%): C, 60.16; H, 7.42; N, 4.13.

Triethyl (*E*)-2-cyano-3-(4-formylphenyl)cyclopropane-1,1,2-tricarboxylate (5g). A colorless oil, n_D^{20} 1.5125. IR (neat), ν/cm^{-1}: 1700 (C=O); 1748 (C=O); 2252 (CN). ^{1}H NMR, δ: 1.12, 1.31 and 1.39 (all t, 3 H each, 3 Me, J = 7.0 Hz); 3.96 (s, 1 H, CH); 4.15, 4.29 and 4.35 (all q, 2 H each, 3 OCH_2, J = 7.0 Hz); 7.57 (d, 2 H, Ar, J = 8.1 Hz); 7.89 (d, 2 H, Ar, J = 8.1 Hz); 10.01 (s, 1 H, CHO). ^{13}C NMR, δ: 13.8, 13.9, 14.1, 30.7, 38.6, 47.6, 62.9, 63.2, 64.3, 112.3, 129.4, 129.6, 129.9, 136.3, 163.0, 163.9, 164.2, 191.3. Found (%): C, 61.92; H, 5.53; N, 3.55. $C_{20}H_{21}NO_7$. Calculated (%): C, 62.01; H, 5.46; N, 3.62.

Triethyl (*E*)-2-cyano-3-(2-furyl)cyclopropane-1,1,2-tricarboxylate (5h). A colorless oil, n_D^{20} 1.4818. IR (neat), ν/cm^{-1}: 1752 (C=O); 2256 (CN). ^{1}H NMR, δ: 1.24, 1.30 and 1.37 (all t, 3 H each, 3 Me, J = 7.0 Hz); 3.85 (s, 1 H, CH); 4.24, 4.26 and 4.31 (all q, 2 H each, 3 OCH_2, J = 7.0 Hz); 6.39 (dd, 1 H, CH, J = 3.3 Hz, J = 3.3 Hz); 6.54 (d, 1 H, CH, J = 3.3 Hz); 7.41 (s, 1 H, CH). ^{13}C NMR, δ: 13.7, 13.9, 14.0, 30.7, 33.1, 47.0, 63.1, 63.3, 64.2, 110.5, 111.0, 112.4, 162.0, 163.1, 163.6. Found (%): C, 58.52; H, 5.41; N, 3.95. $C_{17}H_{19}NO_7$. Calculated (%): C, 58.45; H, 5.48; N 4.01.

Triethyl (*E*)-2-cyano-3-(2-thienyl)cyclopropane-1,1,2-tricarboxylate (5i). A light yellow oil, n_D^{20} 1.5055. IR (neat), ν/cm^{-1}: 1752 (C=O); 2248 (CN). ^{1}H NMR, δ: 1.20, 1.30 and 1.38 (all t, 3 H each, 3 Me, J = 7.0 Hz); 3.96 (s, 1 H, CH); 4.23, 4.27 and 4.33 (all q, 2 H each, 3 OCH_2, J = 7.0 Hz); 7.00 (dd, 1 H, CH, J = 5.1 Hz, J = 3.7 Hz); 7.22 (dd, 1 H, CH, J = 3.7 Hz, J = 1.1 Hz); 7.31 (dd, 1 H, CH, J = 5.1 Hz, J = 1.1 Hz). ^{13}C NMR, δ: 13.7, 13.9, 14.0, 31.9, 34.9, 48.4, 63.0, 63.2, 64.2, 112.5, 126.6, 127.2, 128.0, 162.0, 163.3, 163.8. Found (%): C, 55.81; H, 5.32; N, 3.87, S, 8.69. $C_{17}H_{19}NO_6S$. Calculated (%): C, 55.88; H, 5.24; N, 3.83; S, 8.78.

Hexaethyl 3,3′-(1,4-phenylene)bis[(*E*)-2-cyanocyclopropane-1,1,2-tricarboxylate] (5j). A white powder, m.p. 187—188 °C. IR (KBr), ν/cm^{-1}: 1748 (C=O); 2252 (CN). ^{1}H NMR, δ: 1.15, 1.31 and 1.39 (all t, 3 H each, 3 Me, J = 7.0 Hz); 3.90 (s, 1 H, CH); 4.14, 4.26 and 4.34 (all q, 2 H each, 3 OCH_2, J = 7.0 Hz); 7.42 (s, 4 H, Ar). ^{13}C NMR, δ: 13.8, 13.9, 14.0, 30.7, 30.8, 38.7, 38.8, 47.8, 63.0, 63.2, 64.3, 112.6, 129.2, 130.4, 162.4, 163.7, 164.2. Found (%): C, 59.82; H, 5.80; N, 4.25. $C_{32}H_{36}N_2O_{12}$. Calculated (%): C, 59.99; H, 5.66; N 4.37.

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