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# ALTERNATIVE METHOD FOR SYNTHESIS OF TETRACARBOXYLIC ACIDS WITH CYCLOALIPHATIC FRAGMENTS

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***Abstract.*** *The tetracarboxylic acids containing a cycloaliphatic fragment are promising monomers for semi-aromatic polymers of a series of polyimides, polyesters, and polyetherimides. An alternative method has been developed for their synthesis. The method demonstrates the possibility of performing alkylation and acylation reactions in sequence. The choice of the combination of methods for the oxidation of the acyl and methyl groups has been confirmed by quantum chemical calculations.*

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## Introduction

Highly effective polymers based on semi-aromatic monomers with rigid alicyclic fragments (derivatives of 4-aryl-1,2-norbornane dicarboxylic acid and 4-aryl-1,2-cyclohexanedicarboxylic acid) are of considerable interest for obtaining of new-generation materials. The combination of cycloaliphatic elements in the monomer structure with aromatic substituents and functional groups (carboxyl and carbonyl groups, imide cycle) is used for design of polyesters, polyimideketones and polyetherimideketones, polyimides with a wide range of required properties [1-4]. For example, 4-phenylhexahydro-2-benzofuran-1,3-dione enables obtaining the thermosetting composites for use in displays [5, 6]. Patent [7] describes the use of cycloaliphatic epoxy resins to improve the characteristics of materials used in electronic devices: increasing the glass transition temperature and ensuring a good flat surface. In [4], a composite based on 5-norbornene-2,3-dicarboxylic acid anhydride demonstrated a significant improvement in mechanical properties.

The paper [8] describes the synthesis of a new siloxane-norbornane dianhydride by hydrosilylation of endic acid anhydride with tetramethyldisiloxane. Based on this compound, an epoxy precursor has been developed. The authors claim that the developed material

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combines improved chemical stability, thermal stability and mechanical behaviour, eliminating the problem of phase separation of classical analogues.

The introduction of cyclohexane fragments improves the thermal and mechanical properties of polymers. In addition, polymers with cyclohexane fragments are biodegradable. These results convincingly demonstrate that a simple cyclohexane ring can be used as a biodegradable building block. Those is rigid and exhibits improved thermal and physical properties [9].

The synthesis of arylcycloaliphatic fragments can be performed using alkylation reactions as a method for forming C-C bonds. The paper [10] describes a highly efficient palladium-based catalyst used for the alkylation reaction of phenyl iodide with a wide range of bicyclic alkenes, in particular alkenes with norbornene, norbornadiene, oxa-, and azabicyclic fragments. Such palladium-based catalysts show enormous superiority in many respects due to their stability to air and moisture, the use of catalytic amounts, and high efficiency. In 2015, Miuras et al. [11] reported on a rhodium-catalysed electrophilic substitution reaction with the formation of di-, tri-, and tetra-substituted arenes.

In 2006, the scientists tested the activity of various Lewis and Brønsted acids in the Friedel-Crafts alkylation reaction [12]. According to the studies, transition metal salts, such as $HAuCl_4$, $IrCl_3$, $[MesW(CO)_3]$, $RhCl_3$, $H_2PdCl_4$, $H_2PtCl_6$ and $FeCl_3$, are the most effective ones. Iron chloride is an alternative to rare earth triflates because it is non-toxic, inexpensive, and available [13]. Another example of the use of transition metal salts is the cobalt diphosphine catalyst. It promotes the addition of arylzinc reagent to norbornene derivatives [14].

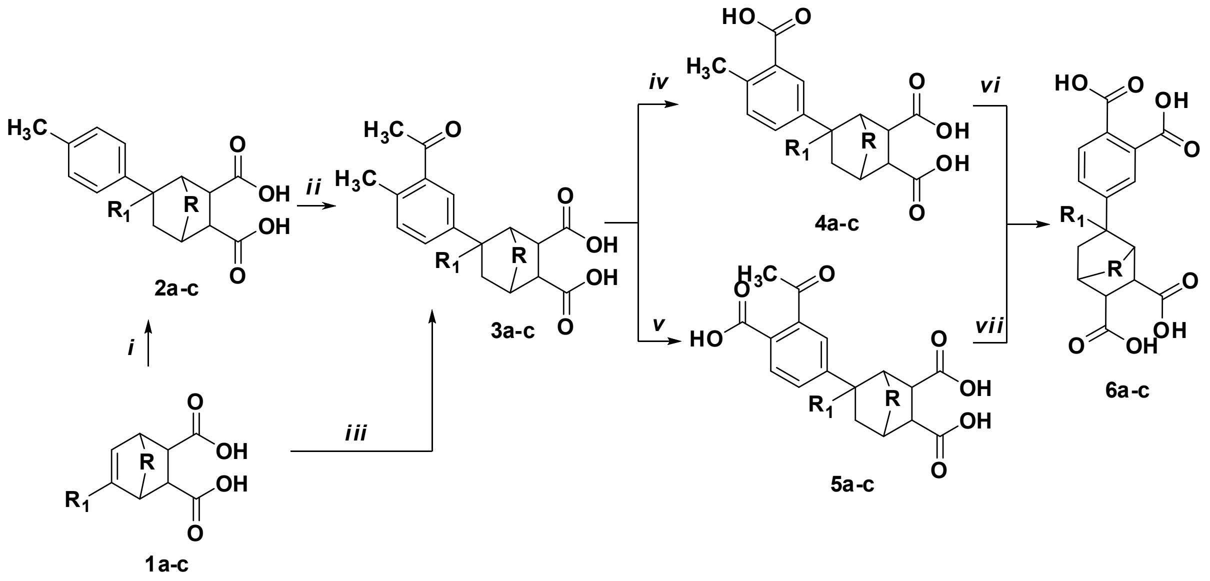
The catalysis of cycloalkenes with aromatic compounds is described using copper salts and can be successfully replaced in the case of expensive palladium-based catalysts [15]. New catalytic approaches, namely alkylation of arenes and heteroarenes according to Friedel-Crafts using only catalytic amounts of Lewis acid, have advantages over the classical Friedel-Crafts reaction conditions, since benzyl, propargyl and allyl alcohols or styrenes can be used instead of toxic benzyl halides [16].

Thus, the development of methods for synthesising new cyclohexane-containing monomers and establishing their basic physicochemical parameters for subsequent use in polycondensation reactions is a relevant issue.

## Main body

Previously, articles [17, 18] described a method for obtaining structures with cycloalkane fragments. We propose an alternative method for synthesising compounds based on a combination of alkylation-acylation reactions and subsequent oxidation (Scheme 1).

4-(3-Acetyl-4-methylphenyl)cycloalkyl dicarboxylic acids **3a-c** were obtained by two methods. The first one includes the sequential interaction of toluene with cycloalkene-1,2-dicarboxylic acids **1a-c** in the presence of a catalyst with the isolation of the resulting 4-methylphenylcycloalkyl dicarboxylic acids **2a-c** and their subsequent reaction with acetyl chloride in the presence of an aluminium chloride catalyst – $AlCl_3$. The yield was 64% in two stages.



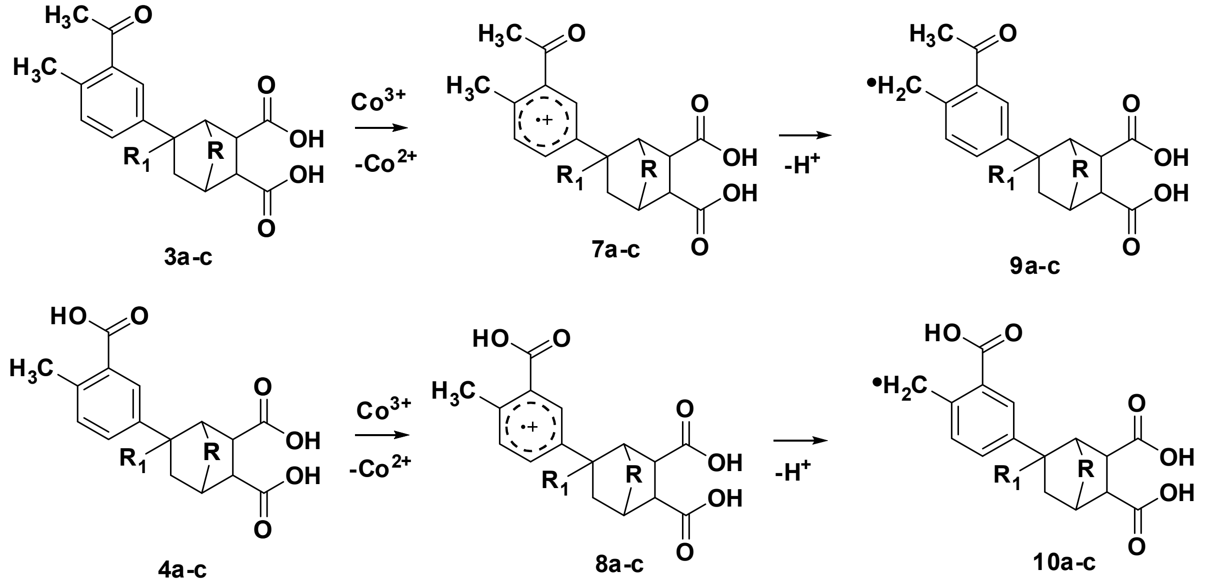
(**a**): R = none, $R_1$ = H; (**b**): R = $CH_2$, $R_1$ = H, (**c**): R = none, $R_1$ = $CH_3$

*i*: PhMe, $AlCl_3$, 40 °C, 4 h; *ii*: AcCl, $CHCl_3$;*iii*:PhMe, $AlCl_3$, AcCl; *v*, *vi*: $O_2$, $Co(AcO)_2$, $Mn(AcO)_2$, NaBr; *iv*, *vii*: NaOH, $Br_2$

**Scheme 1**

The second one was a single-reactor method of alkylation of toluene with cycloalken-1,2-dicarboxylic acids **1a-c** followed by acylation. In this case, an inert solvent, tetrachloroethane, was used. Yield is 60%. The products obtained were purified by recrystallisation from 60% acetic acid.

Then compounds **3a-c** were oxidised: the acetyl fragment was oxidised using the haloform reaction method [17]; and the methyl fragment was oxidised using the liquid-phase oxygen oxidation method in the presence of cobalt and manganese acetate catalysts [18]. The oxidation of 4-(3-acetyl-4-methylphenyl)cycloalkyl dicarboxylic acids **3a-c** with oxygen has a low product yield. Apparently, this is due to the influence of the acetyl group on the formation of ion radicals **7**, **8** (Scheme 2) in the liquid-phase oxidation reaction. In general terms, the $Co^{3+}$ oxidation reaction can be represented as follows [19]:



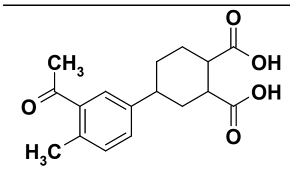
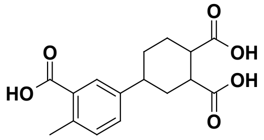
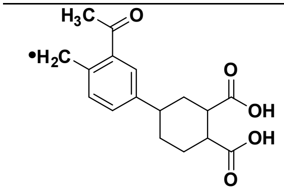
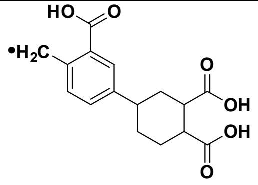
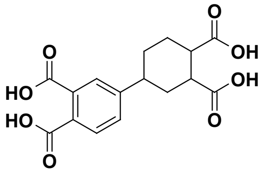
(**a**): R = none, $R_1$ = H; (**b**): R = $CH_2$, $R_1$ = H, (**c**): R = none, $R_1$ = $CH_3$

**Scheme 2**

To confirm this hypothesis, quantum chemical calculations of the energies of the initial, intermediate compounds, and products were performed. The B3LYP electron density functional method [20] was used to calculate the structures, applying the 6-311G(d,p) triple basis set. The molecular structures were optimised; after the thermodynamic parameters for all optimised geometries were sequentially evaluated.

The thermodynamic probability of the oxidation reaction of compounds **3a** and **4a** to compound **6a** was evaluated using quantum chemical methods: calculations of the electronic structures of molecules, energy, molecular structure, thermochemical properties, and energy characteristics of reactions in the ground and excited states [21]. For analysis, we selected heat of formation ($\Delta H_f$, kcal/mol), total energy ($E_{tot}$, kcal/mol), Gibbs energy ($\Delta G$, kcal/mol), entropy ($\Delta S$, J/(mol·K)). These main characteristics allow us to assess the stability of the compounds formed (Table 1).

**Table 1.** Thermodynamic characteristics of structures **3-4a, 6a, 7-10** (temperature 298.15 K and pressure 101.325 kPa)

| Structure | Total energy $E_{tot}$, kcal/mol·$10^3$ | Enthalpy of formation $\Delta H_f$, kcal/mol·$10^3$ | Gibbs energy $\Delta G$, kcal/mol·$10^3$ | Entropy $\Delta S$, J/(mol·K) |
|---|---|---|---|---|
| <br>Compound **3a** | -650.099 | -649.867 | -649.913 | 152.219 |
| <br>Compound **4a** | -672.639 | -672.421 | -672.466 | 148.614 |
| <br>Compound **9** | -671.629 | -671.428 | -671.474 | 154.670 |
| <br>Compound **10** | -649.1 | -648.884 | -648.93 | 153.721 |
| <br>Compound **6a** | -766.287 | -766.077 | -766.125 | 159.612 |

When comparing the enthalpies of formation of the starting materials, intermediate compounds, and products, the formation of radical **10** is more favourable. The lower enthalpy for compound **3a** can be interpreted as the possibility of faster product formation and, as a result, higher product yield. These agree with the experimental data.

To confirm the existence of the transition state, internal coordinate reaction (IRC) calculations were performed. It allows us to investigate the configuration of the energy landscape around the transition point [22, 23]. The transition state was characterised by the presence of a single negative eigenvalue of the Hessian matrix only for compound **4a**. However, the corresponding eigenvector clearly reflects the displacement along the reaction coordinate. The transition state was localised using the TS (Transition State) method algorithm [24].

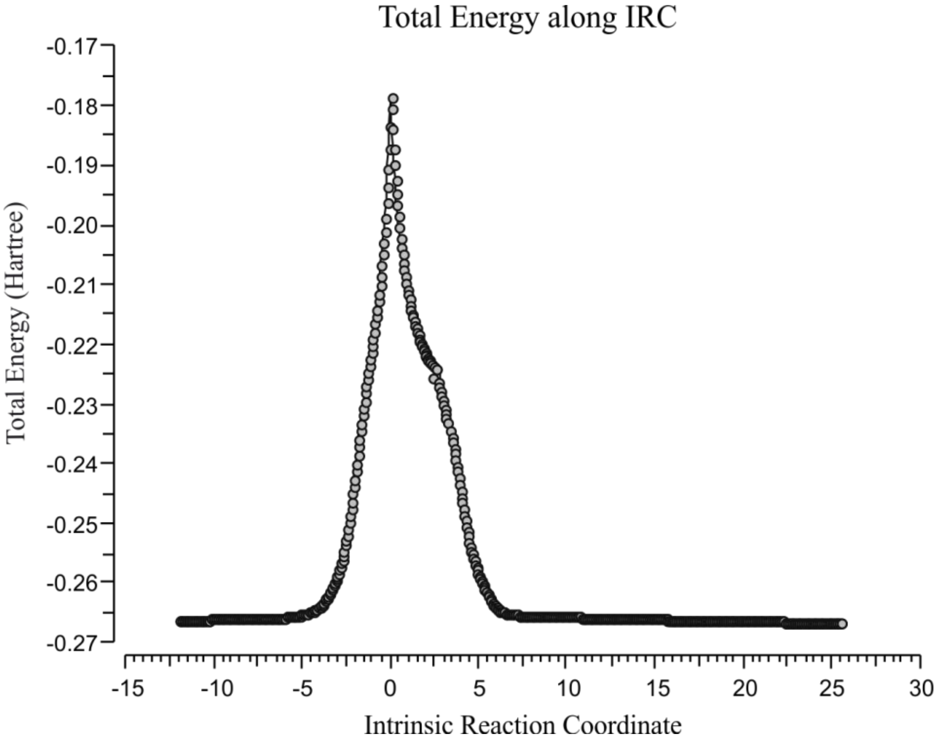


**Fig. 1.** Procedure for restoring the reaction coordinate using the IRC method of connection **4a**

According to reaction pathways analysis and final structures of the IRC procedure, the reaction is single-stage one and does not involve any intermediates other than weakly bound pre-reaction and post-reaction complexes.

We conducted a study on the effect of reaction time on the yield of oxidation product **6a**. The reaction was conducted at a temperature of 90 °C; a reaction time is 3 hours. Samples were taken every half hour and analysed by HPLC (Table 2).

**Table 2.** Effect of oxidation reaction time on product **6a** content, %

| Reaction time, h | Composition of reaction mixture, % | |
|---|---|---|
| | Starting material **3a**, % | Reaction product **6a**, % |
| 0.5 | 55 | 45 |
| 1 | 46 | 64 |
| **2** | **0.05** | **99.95** |
| 3 | 0.05 | 99.95 |

According to the Table 2, product formation is observed within 30 minutes; the highest yield is achieved within 2 hours.

## Conclusions

The method for the synthesis of tetracarboxylic acids containing a cycloaliphatic fragment has been developed. It allows products to be obtained with a high yield of 60%. The probability of obtaining tetracarboxylic acids using a single-reactor method has been demonstrated. Based on quantum chemical methods, calculations were performed and the path and sequence of oxidation reactions of methyl and acyl groups were determined. As a result of studying the oxidation reaction, the highest product yield is observed in 2 hours.

### *Experimental part*

Reaction monitoring and identification of synthesised compounds were performed using thin-layer chromatography (TLC) on Kieselgel-G plates (MerckSi 254F). A mixture of petroleum ether, toluene, acetone, and acetic acid in a ratio of 50:30:50:1 (by volume) was used as the eluent.

Infrared (IR) spectra were recorded on a PerkinElmer SpectrumTwo Fourier transform spectrometer using a near-infrared (NIR) probe. The $^1$H and $^{13}$C NMR spectra were recorded on a Varian UNITY plus 400 MHz instrument at 303 K. All compounds were analysed as 5% solutions in DMSO-d$_6$ with tetramethylsilane (TMS) as an internal standard. The chemical shifts of $^1$H NMR are given relative to the residual signal (δH 2.5 ppm). The chemical shifts of $^{13}$C NMR are given relative to the central signal of the solvent (δC 39.5 ppm). The melting temperatures of the compounds were determined using an Electrothermal IA 9300 Series instrument. High-resolution mass spectra were recorded on a BrukermicrOTOF II device with electrospray ionisation (ESI). Reagents and solvents (Aldrich, Acros) are commercially available and were used without prior purification.

The synthesis methods and physicochemical characteristics of compounds **2a-c** and **6a-c** are described in [17,18].

**Synthesis of 4-(3-acetyl-4-methylphenyl)cycloalkyl dicarboxylic acids. General methodology**

10 ml of chloroform and 0.5 g (1.81 mmol) of compound **4-6** are loaded into a flask equipped with a refrigerator and a stirrer. Then we add 1 g (7.24 mmol) of aluminium chloride in portions at a temperature of 50 °C, followed by 0.2 ml (2.17 mmol) of acetyl chloride. We stir it for 4 hours at a temperature of 50 °C. The reaction mixture is precipitated in ice water and 5 ml of 36% hydrochloric acid. The precipitate is filtered and dried. The resulting product is purified by crystallisation from an aqueous solution of acetic acid.

**Synthesis of 4-(3-acetyl-4-methylphenyl)cycloalkyl dicarboxylic acids. Single-reactor method**

10 ml of tetrachloroethane and 0.5 g (2.74 mmol) of compound **1-3** are loaded into a flask equipped with a refrigerator and a stirrer. At a temperature of 50 °C, 1.1 g (8.24 mmol) of aluminium chloride is added in portions and stirred for 2 hours; then 0.36 g (2.74 mmol) of aluminium chloride and 0.2 ml (2.17 mmol) of acetyl chloride are added. We stir it for 2 hours at a temperature of 50 °C. The reaction mixture is precipitated in ice water and 5 ml of 36% hydrochloric acid. The precipitate is filtered and dried. The resulting product is purified by crystallisation from an aqueous solution of acetic acid.

**4-(3-Acetyl-4-methylphenyl)cyclohexane-1,2-dicarboxylic acid (3a)**. Yield is 80%. $T_{melt.}$ is 180-182 °C. IR-spectrum, ν/cm$^{-1}$: 2950, 2856(ν$CH_2$, ν$CH_3$), 2730, 2678, 2542(OH), 1720 (C=O, ketone), 1698 (C=O, acid), 1603 (Ar), 1223, 1209 (C-O), 925 (OH), 880, 816 (1,2,4-substitution). NMR-spectrum $^1$H (DMSO-d6, δ, ppm, *J*/Hz): 12.13 (br.s, 2H, COOH), 7.71 (t, *J* = 8.4 Hz, 2H, Ar), 7.17 (d, *J* = 8.4 Hz, 1H, Ar), 7.11 (d, *J* = 8.4 Hz, 3H, C(O)C$\underline{H}_3$), 2.72-2.64 (m, 1H, CH), 2.04-1.72 (m, 1H, CH), 2.12-2.10 (m, 2H, $CH_2$), 1.93-1.89 (m, 1H, CH), 1.64-1.51 (m, 1H, CH), 1.49-1.46 (m, 2H, $CH_2$), 1.35-1.27 (m, 1H, CH), 1.07-1.05 (m, 3H, $CH_3$). NMR-spectrum $^{13}$C (100 MHz, δ, ppm): 175.23, 174.95, 146.82, 138.83, 129.77, 127.81, 127.48, 126.55, 126.45, 124.75, 37.87, 36.55, 36.03, 32.43, 31.59, 23.69, 21.82. Mass-spectrum (EI, 70 eV), *m/z* ($I_{rel}$,%): 332 (28), 229 (59), 257 (32), 212 (100), 197 (25), 169 (35), 145 (30), 43 (30). Mass-spectrum (ESI), *m/z*: found for $C_{17}H_{20}O_5$: 304.1311, calculated for $C_{17}H_{20}O_5$: 304.1335.

**5-(3-Acetyl-4-methylphenyl)bicyclo[2.2.1]heptane-2,3-dicarboxylic acid (3b)** Yield is 81%. $T_{melt.}$ is 101-103 °C. IR, ν/cm$^{-1}$: 2964, 2921, 2882 (ν$CH_2$, ν$CH_3$), 2741, 2688, 2552 (OH), 1717 (C=O, ketone), 1709 (C=O, acid), 1605 (Ar), 1228, 1199 (C-O),928 (OH), 864, 811 (1,2,4-substitution). NMR-spectrum $^1$H (DMSO-d6, δ, ppm, *J*/Hz): 12.03 (br.s, 2H, COOH), 7.16 (t, *J* = 7.5 Hz, 1H, Ar), 7.09 (d, *J* = 8.4 Hz, 1H, Ar), 7.06-6.99 (m, 3H, C(O)C$\underline{H}_3$), 6.95 (d, *J* = 7.4 Hz, 1H, Ar), 3.03-2.99 (m, 2H, $CH_2$), 2.89 (m, 2H, $CH_2$), 2.42-2.37 (m, 2H, CH2), 2.06-2.01 (m, 1H, CH), 1.55 (m, 3H, $CH_3$), 1.38-1.35 (m, 1H, CH), 1.19-1.15 (m, 1H, CH). NMR-spectrum $^{13}$C (100 MHz, δ, ppm):174.23, 173.93, 147.02, 137.83, 129.47, 128.81, 128.38, 127.53, 126.75, 124.69, 47.87, 46.55, 46.03, 42.43, 41.59, 37.34, 33.69, 21.82. Mass-spectrum (EI, 70 eV), *m/z* ($I_{rel}$, %):344 (5), 271 (10), 256 (32), 242 (25), 183 (13), 156 (100), 141 (13), 128 (17), 113 (23), 91 (16). Mass-spectrum (ESI), *m/z*: found for $C_{17}H_{20}O_5$: 316.1311, calculated for $C_{17}H_{20}O_5$: 316.1345.

**4-(3-Acetyl-4-methylphenyl)-4-methylcyclohexane-1,2-dicarboxylic acid (3c)**. Yield is 86%. $T_{melt.}$ is 125-127°C. IR, ν/cm$^{-1}$: 2918, 2988 (ν$CH_2$, ν$CH_3$), 2745, 2679, 2547 (OH), 1718 (C=O, ketone), 1705 (C=O, acid), 1605 (Ar), 1223, 1210 (C-O), 945 (OH), 882, 816 (1,2,4-substitution). NMR-spectrum $^1$H (DMSO-d6, δ, ppm, *J*/Hz): 12.13 (br.s, 2H, COOH), 7.24-7.20 (m, 2H, Ar), 7.14 (d, *J* = 7.3 Hz, 3H, C(O)C$\underline{H}_3$), 6.98 (d, *J* = 6.5 Hz, 1H), 2.86 (s, 1H, CH), 2.31-2.27 (m, 2H, $CH_2$), 2.26-2.27 (m, 2H, $CH_2$), 2.10-2.07 (m, 2H, $CH_2$), 1.93-1.91 (m, 3H, $CH_3$), 1.21-1.18 (m, 1H, CH), 1.09-1.05 (m, 3H, $CH_3$). NMR-spectrum $^{13}$C (100 MHz, δ, ppm): 175.61, 175.46, 146.97, 138.17, 135.08, 129.87, 129.15, 126.89, 126.32, 125.43, 123.47, 38.63, 33.85, 31.33, 30.82, 24.82, 22.03, 21.09. Mass-spectrum (EI, 70eV), *m/z* ($I_{rel}$, %): 342 (5), 271 (10), 242 (48), 183 (17), 156 (100), 145 (13), 113 (22), 91 (12). Mass-spectrum (ESI), *m/z*: found for $C_{18}H_{22}O_5$: 306.1461, calculated for $C_{18}H_{22}O_5$: 306.1467.

**Synthesis of 4-(3-carboxylic-4-methylphenyl)cycloalkyl dicarboxylic acids. General methodology**

At the intensive stirring and cooling to 10 °C. 0.2 g (0.6289 mmol) of compound **7-9** is added to a solution of 4 g of caustic soda in 50 ml of water in a three-necked flask equipped with a stirrer, a dropping funnel and a thermometer. Next, we add 0.15 ml (1.887 mmol) of bromine dropwise and stir for 15 minutes at a temperature of 0-5 °C. Then we leave it at room temperature and stir for 1 hour. Next, we heat it to 50-60 °C for 5 hours. Then we separate the resulting bromoform. We add a 5% aqueous solution of sodium thiosulphate to the alkaline solution and acidify with concentrated hydrochloric acid to a pH of 2-3. The precipitate is filtered and dried.

**4-(3-Carboxy-4-methylphenyl)cyclohexane-1,2-dicarboxylic acid (4a)**. Yield is 81%. $T_{melt.}$ is 183-185°C. IR, $\nu$/cm$^{-1}$: 2950, 2925, 2865 ($\nu CH_2$, $\nu CH_3$), 2655, 2575(OH),1728 (C=O,ketone), 1697, (C=O, acid), 1606 (Ar), 1250 (C-OH),931 (OH), 880, 826 (1,2,4-subtitution). NMR-spectrum $^1$H (DMSO-d6, $\delta$, ppm, J/Hz):12.07 (br.s, 3H, COOH), 7.11 (d, *J* = 8.3 Hz, 1H, Ar), 7.07 (d, *J* = 6.7 Hz, 1H, Ar), 6.98 (d,*J* = 7.4 Hz, 1H, Ar), 2.73-2.69 (m, 1H, CH), 2.49-2.47 (m, 1H, CH), 2.48-2.40 (m, 1H, CH), 2.16-2.07 (m, 2H, $CH_2$), 1.94-1.88 (m, 3H, $CH_3$), 1.63-1.58 (m, 1H. CH), 1.53-1.49 (m, 2H, $CH_2$), 1.37-1.34 (m, 1H, CH), 1.20 (d, *J* = 5.5 Hz, 2H, $CH_2$). NMR-spectrum $^{13}$C (100 MHz, $\delta$, ppm): 175.23, 174.95, 174.85, 130.78, 129.81, 127.83, 126.45, 125.45, 124.83, 37.87, 36.55, 36.03, 32.43, 31.59, 23.69, 21.82. Mass-spectrum (EI, 70 eV), *m/z* ($I_{rel}$, %): 348 (8), 304 (17), 272 (41), 244 (48), 229 (43), 212 (21), 185 (61), 169 (90), 132 (100), 105 (40), 91 (38), 59 (12), 41 (7). Mass-spectrum (ESI), *m/z*: found for $C_{16}H_{18}O_6$: 306.1103, calculated for $C_{16}H_{18}O_6$:306.1145.

**5-(3-carboxy-4-methylphenyl)bicyclo[2.2.1]heptane-2,3-dicarboxylic acid (4b).** Yield is 83%. $T_{melt.}$ is 141-143°C. IR, $\nu$/cm$^{-1}$: 2965, 2935, 2885 ($\nu CH_2$, $\nu CH_3$), 2675, 2585, (OH), 1701, 1684 (C=O, acid), 1605 (Ar), 1250 (C-OH), 935(OH), 886, 816 (1,2,4-substitution). NMR-spectrum $^1$H (DMSO-d6, $\delta$, ppm, *J*/Hz): 12.01 (br.s., 3H, COOH), 7.15 (d, *J* = 8.4 Hz, 1H, Ar), 7.09 (d, *J* = 6.4 Hz, 1H, Ar), 6.95 (d, *J* = 7.4 Hz, 1H, Ar), 3.06-2.99 (m, 2H, $CH_2$), 2.91-2.87 (m, 1H, CH), 2.44-2.36 (m, 2H, $CH_2$), 2.25 (s, 1H, CH), 2.67-2.07 (m, 1H, CH), 1.37-1.33 (m, 1H, CH), 1.21-1.15 (m, 1H, CH, CH). NMR-spectrum $^{13}$C (100 MHz, $\delta$, ppm): 174.23, 173.93, 173.55,132.38, 130.47, 129.82, 128.42, 127.33, 126.65, 47.74, 46.75, 46.13, 42.33, 41.69, 37.44, 33.71, 22.82. Mass-spectrum (ESI), *m/z*: found for $C_{17}H_{18}O_6$: 318.1110, calculated for $C_{17}H_{18}O_6$: 318.1103.

**4-(3-carboxy-4-methylphenyl)-4-methylcyclohexane-1,2-dicarboxylic acid (4c)**. Yield is 75%. $T_{melt.}$ 147-149°C. IR, $\nu$/cm$^{-1}$: 2950, 2932, 2886 ($\nu CH_2$, $\nu CH_3$), 2665, 2577 (OH), 1707 (C=O, acid), 1601 (Ar), 1250 (C-OH), 932 (OH), 880, 832 (1,2,4-substitution). NMR-spectrum $^1$H (DMSO-d6, $\delta$, ppm, *J*/Hz):12.09 (br.s., 3H, COOH), 7.21 (d, *J* = 6.2 Hz, 1H, Ar), 7.16-7.05 (m, 2H, Ar), 2.84 (s, 1H, CH), 2.26-2.20 (m, 3H, $CH_3$), 2.16-2.05 (m, 2H, $CH_2$), 2.04-1.92 (m, 2H, $CH_2$), 1.54-1.49 (m, 2H, $CH_2$), 1.33-1.27 (m, 1H, CH), 1.25-1.21 (m, 1H, CH), 1.07-1.01 (m, 2H, $CH_2$). NMR-spectrum $^{13}$C (100 MHz, $\delta$, ppm): 175.61, 175.46, 174.76, 138.15, 136.18, 135.87, 129.25, 127.19, 126.34, 124.46, 38.73, 34.95, 31.23, 30.85, 24.85, 22.15, 21.29. Mass-spectrum (ESI), *m/z*: found for $C_{17}H_{20}O_6$: 320.1268, calculated for $C_{17}H_{20}O_6$: 320.1260.

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