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Synthesis and characterization of bola-shaped diester-dicarboxylic compounds

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ABSTRACT

A series of new class of bola-shaped diester-dicarboxylic compounds were synthesized and characterized. Desymmetrization of various anhydrides such as phthalic, succinic and maleic anhydrides using varieties of dihydroxy compounds such as 1,4-butane diol, 1,4-butyne diol, 1,6-hexane diol and 1,4-cyclohexanedimethanol were shown to provide a series of diester-dicarboxylic compounds with good yield. Length and flexibility of the spacer and head groups of these diester-dicarboxylic acid are varied by appropriately adapting suitable diol spacer possessing four carbon flexible alkyl group in "a" and unsaturated rigid alkenyl chain with four carbon spacer in "b" while the same is expanded to six carbon in "c" and "d". Similarly the head groups of these bola shaped compounds were altered using phthalic, succinic and maleic anhydrides (aromatic, saturated and unsaturated). All these compounds were characterized using elemental analysis, and various spectroscopic techniques such as Nuclear Magnetic Resonance, Infrared Spectroscopy and ESI-Mass Spectroscopy.

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KEYWORDS

Dicarboxylic acids;
Bolaamphiphile;
Desymmetrization;
Anhydride;
Helices.

INTRODUCTION

Diester-dicarboxylic compounds had gained significant importance, due to their potentiality for the formation of macrocyclic dilactones^[1-5] and tetralactones. Understanding the importance of the diester-dicarboxylic compounds, researchers in this area are constantly attempted to synthesis these compounds, adapting various synthetic methodologies^[6-9]. Among the synthetic method, the synthetic strategy involving desymmetrization^[10,11] of cyclic anhydride using dihydroxy compounds is considered to be superior method because of its high yield.

With an understanding on the COOH-COOH intermolecular association, we recently demonstrated that these diester-dicarboxylic compounds are potential compounds for the formation of hollow microtubes by introducing appropriate spacer moiety through its self assembly process^[12]. In continuation of that, we further illustrated them recently for the formation of some interesting paddle wheel dimeric Cu₂ compounds^[13]. Thus these bola-shaped diester-dicarboxylic compounds possessing exodentate carboxylic acid head groups is demonstrated for the formation of varieties of self-assembled nano-structures and novel binuclear paddle wheel dimeric Cu(II) metallomacrocyclic complexes.

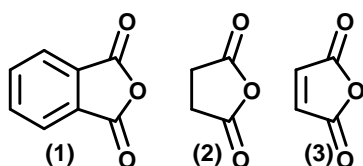


Figure 1 : Anhydrides used as head groups. (1) Phthalic anhydride, (2) Succinic anhydride, (3) Maleic anhydride

Further our recent investigation explores the synthesis of some interesting macrocyclic compounds using the same diester-dicarboxylic compounds^[10]. In this series the bolaamphiphiles reported by Schimizu et al.^[14,15] are well documented in the literature for its capability to provide varieties of nano-assembly^[16-21] which provides variety of potential materials such as gels, micelles, fibers and crystals etc. The strong dimeric COOH-COOH interaction in these molecules interestingly provides variety of superstructures such as helix, knots, etc. Thus the dicarboxylic compounds possessing various potential applications, we inspired to synthesis varieties of some new diester-dicarboxylic compounds, following the desymmetrization method in a view to enrich these versatile organic molecules. Carboxylic acid being multidentate ligand, their coordination with metal ion leads into varieties of metal complexes.

RESULTS AND DISCUSSION

Synthesis

Diester-dicarboxylic compounds depicted in TABLE 1 are synthesized and characterized using various spectroscopic techniques such as NMR, IR and MS. All these compounds possess two terminal carboxylic head groups and the diol spacers in common. The diol spacers and head groups are appropriately changed in such a way to expand the various lengths of diester-dicarboxylic compounds. The spacer moiety possessing ester functional group, the length of the hydrophobic spacer increased four to six carbon moieties upon introducing the compounds (**a-d**) as shown in Figure 2. Phthalic anhydride being head group upon introducing spacer moiety 1,4-butane diol (**a**), 1,4-butyne diol (**b**), and 1,6-hexane diol (**c**) and 1,4-cyclohexane dimethanol (**d**), were systematically varied to obtain compound (**1a**), (**1b**), (**1c**) and (**1d**) to alter the length between the head groups of the bola-shaped compounds. The addition of anhydrides (shown in Figure

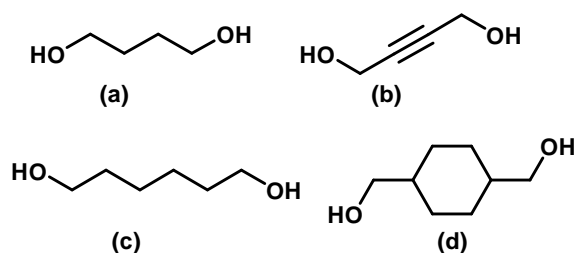


Figure 2 : Dihydroxy compounds used as spacer moiety. (a) 1,6-Hexane diol, (b) 1,4-Butyne diol (c), 1,4-Butane diol (d), 1,4-Cyclohexane dimethanol

1) into diols (shown in Figure 2) in 2:1 ratio, in presence of tetraethylamine results into these diester-dicarboxylic organic compounds as depicted in TABLE 1. All these compounds are isolated as solid powder. The dicarboxylic moieties at the terminal positions are bridged through diols, such as 1,4-butane diol, 1,4-butyne diol, 1,6-hexane diol and 1,4-cyclohexane dimethanol.

Phthalic, succinic and maleic anhydrides are used as aromatic, saturated and unsaturated head groups respectively. Compound (**1a**), (**1b**), (**1c**) and (**1d**) were obtained upon adding phthalic anhydride with 1,4-butane diol, 1,4-butyne diol, 1,6-hexane diol and 1,4-cyclohexane dimethanol respectively. Similarly, upon treating succinic and maleic anhydride, the similar spacers provide compound (**2a-2d**) and (**3a-3d**) respectively, while highest yield 90-96% was obtained in compound (**1c**) and (**1d**), the compounds (**2b**) and (**3a**) were obtained in lowest yield (77%).

Crystal structure of (**1c**)

A further confirmation was made using single crystal obtained for the compound (**1c**). ORTEP diagram with atom numbering scheme for representative compound (**1c**) is given in Figure 3. The crystallographic data is presented in Ref. 22. Compound (**1c**) possessing flexible hexamethylene spacer and two terminal

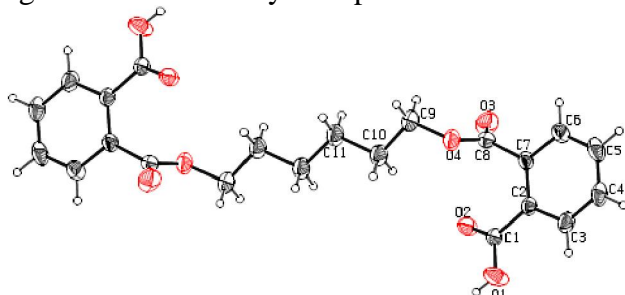


Figure 3 : ORTEP diagram of the compound (1c**) with the atom numbering scheme (30% probability factor for the thermal ellipsoids)**

Full Paper

phthalyl moieties, they are oriented opposite to each other. The terminal carboxylate oxygen O_1 and O_2 mediates a strong O-H...O, H-bond, with O_2 and O_1 of the next neighboring molecule from either end and forms COOH-COOH mediated single stranded supramolecular helical architecture. [Details of this H-bonding interactions is $O_1-H_1...O_2 : H_1...O_2 = 1.813\text{\AA}$; $O_1-H_1...O_1 = 2.6683\text{\AA}$; and $\angle O_1-H_1...O_2 = 176.99^\circ$].

CONCLUSION

In conclusion, we have synthesized a series of bola-shaped diester-dicarboxylic acids. The desymmetrization of various anhydrides, such as phthalic, succinic and malice adapting appropriate diols such as 1,4-butane diol, 1,4-butene diol, 1,6-hexane diol and 1,4-cyclohexanedimethanol was demonstrated without any ambiguity. These compounds possessing end carboxylic acids in their terminal moiety, the variation in their spacer with rigid and flexible nature, gives special recognition for its application in the construction of supramolecular network, such as helices macrocycles, metallomacrocycles, MOFs etc and the work in this direction is under progress.

EXPERIMENTAL

All reagents were of commercial quality (Aldrich) and were used as received. Solvents were dried and purified using standard techniques. Reactions were monitored by thin layer chromatography on silica all reaction was carried out under an atmosphere of nitrogen. IR spectra were recorded using KBr pellets on a Perkin-Elmer Spectrum GX FT-IR spectrometer. High-resolution mass analyses were performed using positive electron spray ionization (ESI) technique on a Water QT of -micro mass spectrometer. Elemental analytical data were recorded on a Perkin-Elmer 4100 elemental analyzer. ^1H and ^{13}C NMR spectra were recorded (500 and 125 MHz respectively) on a BRUKER AVANCE II 500 NMR spectrometer using Methanol- D_4 or CDCl_3 . All ^1H NMR Spectra were calibrated with respect to TMS and TMS was used as an internal reference for solvents such as CDCl_3 and CD_3OD . Carbon type were determined from ^{13}C NMR experiments.

General procedure for the bolaamphiphilic dicarboxylic acid synthesis

Anhydride (0.02mol) and diol (0.01mol) in dry dichloromethane were mixed homogeneously in 2:1 ratio under nitrogen atmosphere. The reaction mixture was thermostated at 0°C and 0.06mol of triethylamine (TEA) added. The whole reaction mass was allowed to continue in the same condition for 3h with constant stirring. The thermostat was removed and continued with constant stirring for overnight at room temperature. After all the anhydride was reacted, the solvent was evaporated. The residue was cooled again at 0°C and added 200mL of saturated NaHCO_3 solution in fractions and extracted with ether. The aqueous layer was cooled and acidified using dilute HCl with constant stirring till the effervescence stops. The precipitate obtained was filtered, washed by water thoroughly and dried.

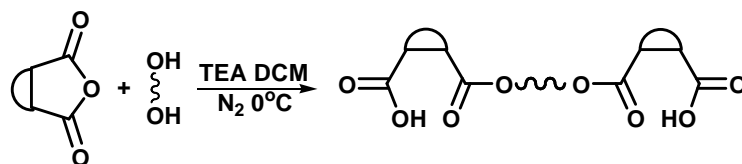
2-((4-[(2-carboxybenzoyl)oxy]butoxy)carbonyl)benzoic acid (1a)

^1H NMR (CDCl_3 , 500.13MHz) δ : 7.51 (b, 2H, OH), 7.53-7.82 (m, 8H, Ar-H), 4.35-4.37 (t, 4H, $-\text{CH}_2$), 1.89-1.90 (t, 4H, $-\text{CH}_2$); ^{13}C NMR. (CDCl_3 , 125.76MHz) δ : 174.49 (C = O), 167.64 (C = O), 128.77 (quat -C), 129.33 (quat -C), 129.70 (= CH), 130.94 (= CH), 131.37 (= CH), 131.82 (= CH), 65.56 ($-\text{OCH}_2$), 24.91 ($-\text{CH}_2$). IR spectral data: (v/cm^{-1}) 3438, 3236, 2644, 1957, 1757, 1732, 1598, 1489, 1451, 1392, 1247, 1130, 1074, 1039, 938, 743. MS (ESI⁺): Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_8\text{Na}$ (M+Na⁺): 409, Found: 409.28. Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_8$ C, 62.17; H, 4.70; Found: C, 62.21; H, 4.62.

2-[(4-[(2-carboxybenzoyl)oxy]but-2-ynyl)oxy]carbonyl]benzoic acid (1b)

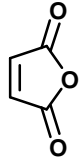

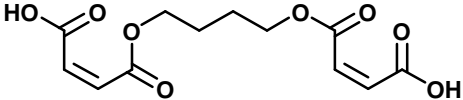
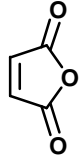

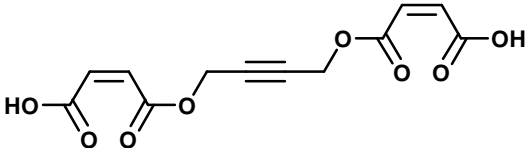
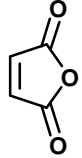

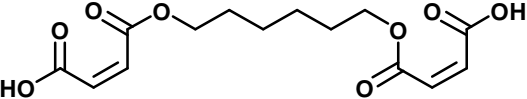
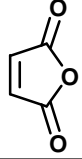
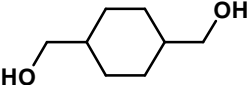
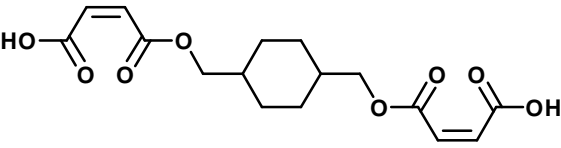
^1H NMR (CDCl_3 , 500.13MHz) δ : 7.57 (b, 2H, OH), 7.27-7.84 (m, 8H, Ar-H), 1.89-1.90 (t, 4H, $-\text{CH}_2$), 4.35-4.37 (t, 4H, $-\text{CH}_2$); ^{13}C NMR. (CDCl_3 , 125.76MHz) δ : 173.79 (C = O), 167.09 (C = O), 132.19 (quat -C), 131.82 (quat -C), 131.86 (= CH), 131.44 (= CH), 130.82 (= CH), 129.36 (= CH), 80.22 ($-\text{C}=\text{C}-$), 53.12 ($-\text{CH}_2$). IR spectral data: (v/cm^{-1}), 3447, 2991, 2856, 2683, 2559, 2113, 1755, 1731, 1696, 1598, 1580, 1494, 1428, 1372, 1315, 1285, 1152, 951, 764, 649. MS (ESI⁺): Calcd. for $\text{C}_{20}\text{H}_{14}\text{O}_8\text{Na}$ (M+Na⁺): 405.00, Found: 405.11. Anal.

TABLE 1 : Syntheses of bolaamphiphile like diacids with various spacer and head groups



Entry	Anhydrides	Diol	Bolaamphiphilic diacids	Yield %
1a				87
1b				92
1c				96
1d				95
2a				93
2b				80
2c				88
2d				94

Full Paper

Entry	Anhydrides	Diol	Bolaamphiphilic diacids	Yield %
3a				77
3b				88
3c				91
3d				90

Calcd. for $C_{20}H_{14}O_8$ C, 62.83; H, 3.69; Found: C, 62.58; H, 3.74.

2-({6-[(2-carboxybenzoyl)oxy]hexanoyl}carbonyl)benzoic acid (1c)

1H NMR ($CDCl_3$, 500.13MHz) δ : 8.87 (b, 2H, OH), 7.57-7.93 (m, 8H, Ar-H), 4.36-4.39 (t, 4H, -OCH₂), 1.77 (s, 4H, -CH₂), 1.52 (s, 4H, -CH₂); ^{13}C NMR. ($CDCl_3$, 125.76MHz) δ : 173.46 (C = O), 168.18 (C = O), 133.80 (quat -C), 132.41 (quat -C), 130.65 (= CH), 129.81 (= CH), 129.53 (= CH), 128.79 (= CH), 65.56 (-OCH₂), 28.14 (-CH₂), 25.42 (-CH₂). IR spectral data: (ν/cm^{-1}), 3449, 2959, 2916, 2858, 2670, 2552, 2359, 1737, 1690, 1598, 1579, 1492, 1469, 1420, 1286, 1256, 1256, 1145, 1119, 1074, 945, 848, 786, 739, 685. MS (ESI⁺): Calcd. for $C_{22}H_{22}O_8Na$ (M+Na⁺): 437, Found: 437.21. Anal. Calcd. for $C_{22}H_{22}O_8$ C, 63.76; H, 5.35; Found: C, 63.53; H, 5.24.

2-({4-[(2-carboxybenzoyl)oxymethyl]-cyclohexyl-methoxy}carbonyl)benzoic acid (1d)

1H NMR ($CDCl_3$, 500.13MHz) δ : 7.54-7.87 (m, 8H, Ar-H), 4.22-4.24 (t, 4H, -OCH₂), 1.21-1.86 (m, 10H, -CH₂) cyclohexane; ^{13}C NMR. ($CDCl_3$, 125.76MHz) δ : 174.31 (C = O), 167.34 (C = O), 132.52 (quat -C), 132.14 (quat -C), 130.66 (= CH),

130.00 (= CH), 129.71 (= CH), 128.84 (= CH), 70.50 (-OCH₂), 37.13 (-CH), 28.73 (-CH₂), 24.40 (-CH₂). IR spectral data: (ν/cm^{-1}) 3478, 3030, 2922 2558, 2363, 1743, 1689 1598, 1492, 1422, 1283, 1249, 1125. MS (ESI⁺): Calcd. for $C_{24}H_{24}O_8Na$ (M+Na⁺): 463, Found 463.33. Anal. Calcd. for $C_{24}H_{24}O_8$ C, 65.45; H, 5.49; Found: C, 65.21; H, 5.39.

4-({4-[(3-carboxypropanoyl)oxy]butoxy}-4-oxobutanoic acid (2a)

1H NMR ($CDCl_3$, 500.13MHz) δ : 6.01 (b, 2H, OH), 4.14 (s, 4H, -OCH₂), 2.63-2.69 (m, 8H, -CH₂), 1.66 (s, 4H, -CH₂); ^{13}C NMR. ($CDCl_3$, 125.76MHz) δ : 178.36 (C = O), 171.78 (C = O), 64.36 (-OCH₂), 29.36 (-CH₂), 29.26 (-CH₂), 25.19 (-CH₂). IR spectral data: (ν/cm^{-1}) 3430, 3041, 2964, 2770, 2685, 2593, 2362, 2206, 1722, 1696, 1401, 1366, 1344, 1249, 1204, 1176, 932. MS (ESI⁺): Calcd. for $C_{12}H_{18}O_8Na$ (M+Na⁺): 313, Found: 313.23. Anal. Calcd. for $C_{12}H_{18}O_8$ C, 49.65; H, 6.25; Found: C, 49.61; H, 6.12.

4-({4-[(3-carboxypropanoyl)oxy]but-2-ynyl}oxy)-4-oxobutanoic acid (2b)

1H NMR ($CDCl_3$, 500.13MHz) δ : 4.75 (s, 4H, -OCH₂), 2.68-2.69 (d, 4H, -CH₂); ^{13}C NMR. ($CDCl_3$, 125.76MHz) δ : 178.11 (C = O), 170.09 (C = O),

80.02 (-C = C-), 50.21 (-OCH₂), 27.51 (-CH₂). IR spectral data: (v/cm⁻¹) 3454, 3054, 2944, 2764, 2666, 2544, 2361, 1734, 1697, 1449, 1411, 1386, 1354, 1327, 1263, 1227, 1170, 959, 891, 843, 812, 650. MS (ESI⁺): Calcd. for C₁₂H₁₄O₈Na (M+Na⁺): 309, Found: 309.48. Anal. Calcd. for C₁₂H₁₄O₈ C, 50.35; H, 4.93; Found: C, 50.45; H, 4.78.

4-((6-[(3-carboxypropanoyl)oxy]hexyl)oxy)-4-oxobutanoic acid (2c)

¹H NMR (CDCl₃, 500.13MHz) δ: 8.31 (b, 2H, OH), 4.13-4.16 (t, 4H, -CH₂), 2.68-2.71 (q, 4H, -CH₂), 2.60-2.63 (q, 4H, -CH₂), 1.61 (s, 4H, -CH₂), 1.36-1.37 (t, 4H, -CH₂); ¹³C NMR. (CDCl₃, 125.76MHz) δ: 178.69 (C = O), 171.89 (C = O), 64.66 (-OCH₂), 29.37 (-CH₂), 28.78 (-CH₂), 25.86 (-CH₂). IR spectral data: (v/cm⁻¹) 3047, 2963, 2873, 2735, 2672, 2360, 1726, 1707, 1477, 1413, 1371, 1322, 1189, 984, 921, 806, 647. MS (ESI⁺): Calcd. for C₁₄H₂₂O₈Na (M+Na⁺): 341, Found: 341.16. Anal. Calcd. for C₁₄H₂₂O₈ C, 52.82; H, 6.97; Found: C, 52.73; H, 6.71.

4-[(4-[(3-carboxypropanoyl)oxy]methyl)cyclohexyl]methoxy]-4-oxobutanoic acid (2d)

¹H NMR (CDCl₃, 500.13MHz) δ: 9.01-9.78 (b, 2H, OH), 3.95-3.96 (d, 4H, -OCH₂), 2.68-2.69 (d, 4H, -CH₂), 2.63-2.64 (d, 4H, -CH₂), 1.78-1.79 (d, 2H, -CH), 1.02-1.63 (m, 8H, -CH₂); ¹³C NMR. (CDCl₃, 125.76MHz) δ: 178.29 (C = O), 172.28 (C = O), 69.59 (-OCH₂), 37.08 (-CH), 34.29 (-CH), 29.07 (-CH₂), 29.01 (-CH₂), 28.7 (-CH₂), 25.06 (-CH₂). IR spectral data: (v/cm⁻¹) 3660, 3441, 3052, 2935, 2855, 2733, 2676, 2632, 2361, 1728, 1702, 1435, 1422, 1323, 1166. MS (ESI⁺): Calcd. for C₁₆H₂₄O₈Na (M+Na⁺): 367, Found: 367.17. Anal. Calcd. for C₁₆H₂₄O₈ C, 55.81; H, 7.02; Found: C, 55.62; H, 6.90.

4-(4-[(3-carboxyprop-2-enoyl)oxy]butoxy)-4-oxobut-2-enoic acid (3a)

¹H NMR (CDCl₃, 500.13MHz) δ: 9.55-9.95 (b, 2H, OH), 6.40-6.42 (d, 2H, -CH = CH-), 6.27-6.30 (d, 2H, -CH = CH-), 4.26 (s, 4H, -O-CH₂), 1.80 (s, 4H, -CH₂); ¹³C NMR. (CDCl₃, 125.76MHz) δ: 169.85 (C = O), 165.445 (C = O), 131.42 (-CH =), 129.41 (-CH =) 65.67 (-OCH₂), 25.15 (-CH₂). IR spectral

data: (v/cm⁻¹) 2970, 2363, 1721, 1692, 1435, 1360, 1277, 1228, 1168, 1028, 923, 861, 814. MS (ESI⁺): Calcd. for C₁₂H₁₄O₈Na (M+Na⁺): 309, Found: 309.37. Anal. Calcd. for C₁₂H₁₄O₈ C, 50.35; H, 4.93; Found: C, 50.43; H, 4.81.

4-[(4-[(3-carboxyprop-2-enoyl)oxy]but-2-ynyl)oxy]-4-oxobut-2-enoic acid (3b)

¹H NMR (CD₃OD, 500.13MHz) δ: 6.28-6.40 (m, 4H, CH = CH), 4.20-4.21 (t, 4H, -CH₂), ¹³C NMR. (CD₃OD, 125.76MHz) δ: 170.17 (C = O), 132.82 (-CH =), 129.40 (-CH =), 84.39 (-OCH₂), IR spectral data: (v/cm⁻¹) 3436, 3101, 2925, 2848, 2715, 2516, 2036, 1738, 1694, 1447, 1402, 1169, 1021, 864, 758, 595, 525. MS (ESI⁺): Calcd. for C₁₂H₁₀O₈Na (M+Na⁺): 305, Found: 305.13. Anal. Calcd. for C₁₂H₁₀O₈ C, 51.07; H, 3.57; Found: C, 49.93; H, 3.43.

4-[(6-[(3-carboxyprop-2-enoyl)oxy]hexyl)oxy]-4-oxobut-2-enoic acid (3c)

¹H NMR (CDCl₃, 500.13MHz) δ: 8.89-9.51 (b, 2H, OH), 6.29-6.14 (m, 4H, CH = CH), 4.26-4.28 (t, 4H, -O-CH₂), 1.42-1.73 (t, 8H, -CH₂); ¹³C NMR. (CDCl₃, 125.76MHz) δ: 168.22 (C = O), 166.38 (C = O), 131.74 (= CH), 130.59 (= CH), 66.10 (-OCH₂), 28.33 (-CH₂), 25.68 (-CH₂). IR spectral data: (v/cm⁻¹) 3430, 3068, 2965, 2895, 2872, 2604, 1724, 1697, 1479, 1425, 1364, 1260, 1216, 1645, 1075, 981, 734, 682. MS (ESI⁺): Calcd. for C₁₄H₁₈O₈Na (M+Na⁺): 337, Found: 337.41. Anal. Calcd. for C₁₄H₁₈O₈ C, 53.50; H, 5.77; Found: C, 53.37; H, 5.58.

4-[(4-[(3-carboxyprop-2-enoyl)oxy]methyl)cyclohexyl]methoxy]-4-oxobut-2-enoic acid (3d)

¹H NMR (CDCl₃, 500.13MHz) δ: 6.35-6.44 (m, 4H, CH = CH), 4.11-4.19 (t, 4H, -CH₂), 1.07-1.86 (m, 8H, -CH₂); ¹³C NMR. (CDCl₃, 125.76MHz) δ: 167.39 (C = O), 165.38 (C = O), 135.01 (-CH =), 132.97 (-CH =), 130.70 (= CH), 129.72 (= CH), 71.37 (-OCH₂), 68.93 (-OCH₂), 36.69 (-CH), 33.79 (-CH), 28.54 (-CH₂), 24.84 (-CH₂); IR spectral data: (v/cm⁻¹) 3756, 3422(-OH), 3062, 2929, 2858, 2622, 2531, 2362, 1723, 1693, 1433, 1274, 1169, 1018, 987, 819, 734. MS (ESI⁺): Calcd. for C₁₆H₂₀O₈Na (M+Na⁺): 363, Found: 363.43. Anal. Calcd. for

Full Paper

$C_{16}H_{20}O_8$ C, 56.47; H, 5.92; Found: C, 56.38; H, 5.90.

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