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ORIGINAL ARTICLE

Novel synthesis of resorcinarene *O*-acetates by $BF_3{\cdot}OEt_2$-catalyzed cyclocondensation of 1,3-(dialkoxycarbonylmethoxy)benzenes with aldehydes

Rui Zhou · Jia Chao Ren · Chao Guo Yan

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Abstract Resorcinarene *O*-acetates, which are key intermediates in the chemical modification process of resorcinarene, can be efficiently prepared in high yields by $BF_3{\cdot}OEt_2$ catalyzed cyclocondensation of 1,3-(dialkoxycarbonylmethoxy)benzenes with aromatic or aliphatic aldehydes in CH_2Cl_2 at room temperature. The single crystal structure analysis indicates alkyl resorcinarenes prefer *rccc* configuration, while aryl resorcinarenes usually adopt *rctt* configuration.

Keywords Resorcinarene · Acetate · Alkylation · Configuration · Crystal structure

Introduction

Resorcinarenes are unique three-dimensional cyclic aromatic tetramers, which are easily synthesized by well-established one-pot procedures and are easily available building blocks for the design of various supramolecular arc structures. [1, 2] The presence of a molecular cavity, which varies in size and properties depending on the nature and arrangement of introduced functional groups, indicates their potentially wide usage as receptor systems, and building blocks for even more larger supramolecular assemblies [3–5]. To perform this design, various methods have been developed for complete and selective chemical modifications on the upper rim and lower rim of resorcinarenes. Acylations and alkylations of hydroxyl groups were usually used for the synthesis of cavitands, carcerands, hemicarcerands and molecule capsules [6]. Resorcinarenes are traditionally prepared by the mineral acid-catalyzed condensation of resorcinol with an aliphatic or aromatic aldehyde [7]. A solvent-free synthesis of resorcinarenes using *p*-toluene-sulfonic acid as the catalyst has also been reported [8]. In addition, some conventional Lewis acids like $BF_3{\cdot}OEt_2$, $AlCl_3$, and $SnCl_4$ have been used in the synthesis of aromatic aldehyde-derived resorcinarenes [9, 10]. More recently, ytterbium(III) triflate [11, 12] and bismuth(III) triflate [13, 14], have been described as efficient catalysts for the synthesis of calix[4]resorcinarenes. Their octaether derivatives have also been prepared by the acid-catalyzed condensation of 1,3-dialkoxybenzenes with aldehydes [15, 16]. Furthermore, the acid-catalyzed cyclooligomerization of 2,4-dialkoxycinnamates [17] or 2,4-dialkoxybenzyl alcohols [18, 19] produces the cyclic products. The acid-catalyzed condensation of 2-propylresorcinol with formaldehyde diethyl acetal to form calix[4]resorcinarene, calix[5]resorcinarene, and calix[6]resorcinarene [20, 21]. Our continued interest in the design of new types of valuable receptor molecules for supramolecular structures prompted us to investigate the efficient synthesis of resorcinarene functional derivatives [22, 23]. We initiated a study on the possibility of direct synthesis of functional resorcinarene derivatives, and herein we wish to report our research results of the efficient synthesis and crystal structures of resorcinarene *O*-acetates by $BF_3{\cdot}OEt_2$ catalyzed cyclocondensation reactions of 1,3-(dialkoxycarbonylmethoxy)benzenes with aldehydes.

Experiment section

All reagents and solvents were commercial available with analytical grade and used as received. Further purification

R. Zhou · J. C. Ren · C. G. Yan (✉)
College of Chemistry and Chemical Engineering,
Yangzhou University, 225002 Yangzhou, China
e-mail: cgyan@yzu.edu.cn

and drying by standard method were employed and distilled prior to use when necessary. All evaporations of organic solvents were carried out with a rotary evaporator in conjunction with a water aspirator. Melting points were taken on a hot-plate microscope apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AV-600 spectrometer. IR spectra were obtained on a Bruker Tensor27 spectrometer (KBr disc). X-ray data were collected on a Bruker Smart APEX-2 CCD diffractometer.

General procedure for the synthesis of resorcinarene *O*-acetates

A solution of aldehyde (10.0 mmol) and 1,3-di(alkoxycarbonylmethoxy)benzene **1a–1b** (10.0 mmol) in anhydrous dichloromethane (30 mL) was cooled in ice bath. Boron trifluoride etherate (40.0 mmol, 5.70 g) was added dropwise to the solution and the mixture was stirred at room temperature overnight. The reaction mixture was then washed with water (100 mL), and the organic layer was dried with $CaCl_2$ and the solvent removed under reduced pressure to give a red oil residue. This was dissolved in a minimum amount of hot ethanol that, upon cooling afforded pale plates. Recrystallisation from ethanol and chloroform gave pure products **2a–2m** for analysis.

2a (R = CH_3, R′ = C_2H_5): white solid, Yield: 69%, mp: 111.1–112.6 °C. IR (KBr disc) υ: 2960(m), 1761(vs), 1614(m), 1587(m), 1504(s), 1439(s), 1408(m) 1379(s), 1125(s), 1084(s), 1026(m), 860(w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.11 ~ 7.07 (m, 1H, ArH), 6.65 (s, 2H, ArH), 6.26 (d, J = 4.2 Hz, 1H, ArH), 6.21 (s, 3H, ArH), 6.13 (d, J = 4.8 Hz, 1H, ArH), 4.56 ~ 4.52 (m, 8H, OCH_2), 4.32 ~ 4.25 (m, 10H, OCH_2, CH), 4.09 ~ 3.97 (m, 2H, CH), 3.76 (s, 24H, OCH_3), 1.89 (q, J = 14.4 Hz, 8H, CH_2); 0.95 (t, J = 7.2 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 13.7, 22.3, 27.6, 29.5, 31.6, 31.6, 34.1, 35.2, 51.5, 66.7, 100.3, 126.1, 128.1, 154.1, 169.4.

2b (R = CH_3, R′ = n-C_3H_7): white solid, Yield: 63%, mp: 127.6–128.7 °C. IR (KBr) υ: 3442(w), 2955(m), 2869(m), 1765(vs), 1613(m), 1587(m), 1503(s), 1438(s), 1408(m), 1379(s), 1180(s), 1124(s), 1078(s), 1078(m), 859(w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 6.62 (s, 4H, ArH), 6.21 (s, 4H, ArH), 4.61 (t, J = 6.6 Hz, 4H, CH), 4.28 (s, 16H, OCH_2), 3.76 (s, 24H, OCH_3), 1.84 (q, J = 7.2 Hz, 8H, CH_2), 1.37 (q, J = 7.2 Hz, 8H, CH_2), 0.93 (t, J = 7.2 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$) [ppm]: δ: 14.1, 20.0, 22.6, 27.6, 30.5, 32.0, 34.4, 35.6, 51.9, 67.1, 100.7, 126.5, 128.5, 154.4, 169.8.

2c (R = CH_3, R′ = n-C_5H_{11}): 67%, mp: 103.6–104.7 °C. IR (KBr) υ: 2956(s), 2930(s), 1764(vs), 1612(m), 1587(m), 1503(s), 1439(s), 1407(m), 1379(s), 1130(s), 1083(s), 978(m), 905(m), 830(w) cm^{-1}. ^{1}H NMR($CDCl_3$) δ: 6.61 (s, 4H, ArH), 6.21 (s, 4H, ArH), 4.58 (b, 4H, CH), 4.28 (s, 16H, OCH_2), 3.76 (s, 24H, OCH_3), 1.85 (d, J = 6.0 Hz, 8H, CH_2), 1.29 (s, 24H, CH_2), 0.85 (t, J = 6.0 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 14.1, 22.7, 27.9, 29.5, 29.6, 31.9, 34.5, 35.6, 51.9, 67.1, 100.7, 126.5, 128.5, 154.4, 169.8.

2d (R = CH_3, R′ = n-C_6H_{13}): white solid, 57%, mp: 69.6–70.9 °C. IR (KBr) υ: 2956(s), 2927(s), 1765(vs), 1612(m), 1587(m), 1503(s), 1439(s), 1407(m), 1379(s), 1130(s), 1084(s), 978(m), 905(m), 833(w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.09 ~ 7.05 (m, 1H, ArH), 6.62 (s, 2H, ArH), 6.27 (t, J = 9.0 Hz, 1H, ArH), 6.21 (s, 3H, ArH), 6.13 (d, J = 3.6 Hz, 1H, ArH), 4.59 (b, 4H, CH), 4.28 (b, 10H, OCH_2), 4.12 ~ 3.99 (m, 2H, OCH_2), 3.76 (s, 24H, OCH_3), 1.85 (d, J = 5.4 Hz, 8H, CH_2), 1.33–1.25 (m, 32H, CH_2), 0.85 (t, J = 6.6 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 47.8, 50.9, 51.0, 51.0, 51.1, 65.7, 65.9, 98.0, 99.4, 124.6, 125.5, 126.2, 126.5, 127.9, 127.9, 131.3, 140.9, 153.4, 153.6, 168.3, 168.4, 168.6.

2e (R = CH_3, R′ = n-C_7H_{15}): light white solid, Yield: 72%, mp: 78.4–79.9 °C. IR (KBr) υ: 2956(s), 2927(s), 1765(vs), 1612(m), 1587(m), 1503(s), 1439(s), 1407(m), 1379(s), 1129(s), 1085(s), 979(m), 903(m), 834(w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.11 ~ 7.07 (m, 1H, ArH), 6.61 (s, 2H, ArH), 6.28 ~ 6.26 (m, 1H, ArH), 6.21 (s, 3H, ArH), 6.12 (d, J = 1.8 Hz, 1H, ArH), 4.61 ~ 4.55 (m, 4H, CH), 4.27 (b, 10H, OCH_2), 4.09 ~ 3.97 (m, 2H, OCH_2), 3.75 (s, 24H, OCH_3), 1.32 (s, 16H, CH_2), 1.22–1.26 (m, 32H, CH_2), 0.85 (s, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 14.0, 22.6, 27.9, 29.4, 29.6, 29.9, 31.9, 34.4, 35.6, 51.8, 67.0, 98.2, 99.2, 100.2, 100.6, 126.4, 128.4, 154.3, 169.7.

2f (R = CH_3, R′ = n-C_8H_{17}): light white solid, Yield: 62%, mp: 78.1–79.7 °C. IR (KBr) υ: 2956(s), 2926(s), 1766(vs), 1611(m), 1587(m), 1503(s), 1438(s), 1407(m), 1379(s), 1307(s), 1214(s), 1129(s), 1084(s), 979(m), 904(m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.10 ~ 7.06 (m, 1H, ArH), 6.61 (s, 3H, ArH), 6.27 (s, 1H, ArH), 6.21 (s, 2H, ArH), 6.13 (s, 1H, ArH), 4.59 ~ 4.54 (m, 4H, CH), 4.39 ~ 4.19 (m, 10H, OCH_2), 4.10 ~ 3.97 (m, 2H, OCH_2), 3.76 (s, 24H, OCH_3), 1.82–1.86 (m, 6H, CH_2), 1.23 (b, 50H, CH_2), 0.86 (t, J = 6.6 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 14.1, 22.7, 27.9, 28.0, 29.4, 29.7, 29.8, 30.0, 31.9, 34.5, 35.7, 51.9, 67.1, 100.7, 126.5, 128.5, 154.4, 169.8.

2g (R = CH_3, R′ = n-C_9H_{19}): light yellow solid, Yield: 67%, mp: 81.3–82.9 °C. IR (KBr) υ: 2956(s), 2925(s), 1766(vs), 1611(m), 1587(m), 1503(s), 1438(s), 1407(m), 1379(s), 1307(s), 1213(s), 1129(s), 1084(s), 978(m), 904(m), 827(m), 721(m). ^{1}H NMR ($CDCl_3$) δ: 7.11 ~ 7.07 (m, 1H, ArH), 6.61 (s, 2H, ArH), 6.26 (d, J = 8.4 Hz, 1H, ArH), 6.21 (s, 3H, ArH), 6.12 (s, 1H, ArH), 4.59 ~ 4.54 (m, 4H, CH), 4.38–4.19 (m, 10H, OCH_2), 4.09 ~ 3.96 (m, 2H, CH_2), 3.75 (s, 24H, OCH_3), 1.84 (d, J = 6.0 Hz, 6H, CH_2), 1.23 (b, 58H, CH_2), 0.86 (t, J = 6.6 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 14.0, 22.6, 28.0, 29.4, 29.7, 29.7, 29.9, 31.9, 34.4, 35.6, 51.9, 67.1, 100.7, 126.5, 128.4, 154.4, 169.8.

2h (R = CH_3, R′ = C_6H_5): white solid, Yield: 76%, mp: 81.3–82.9 °C. IR (KBr) υ: 2956(s), 2925(s), 1766(vs), 1611(m), 1587(m), 1503(s), 1438(s), 1407(m), 1379(s), 1307(s), 1213(s), 1129(s), 1084(s), 978(m), 904(m), 827(m), 721(m) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.19 ~ 7.15 (m, 4H, ArH), 7.00–7.08 (m, 3H, ArH), 6.78 (s, 8H, ArH), 6.44 (d, *J* = 3.0 Hz, 3H, ArH), 6.36 (s, 1H, ArH), 6.06 (s, 4H, CH), 4.55 ~ 4.47 (m, 16H, OCH_2), 3.85 (s, 12H, OCH_3), 3.81(s, 12H, OCH_3); ^{13}C NMR ($CDCl_3$) δ: 14.0, 22.6, 28.0, 29.4, 29.7, 29.7, 29.9, 31.9, 34.4, 35.6, 51.9, 67.1, 100.7, 126.5, 128.4, 154.4, 169.8.

2i (R = CH_3, R′ = $C_6H_4CH_3$-*p*): white solid, Yield: 56%, mp: 187.3–188.5 °C. IR (KBr) υ: 2954 (w), 1738(vs), 1589(m), 1500(s), 1438(m), 105(w), 1113(s), 1078(s), 928(w), 848(w), 701(s) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 6.85 (d, *J* = 7.8 Hz, 2H, ArH), 6.75 (d, *J* = 7.8 Hz, 8H, ArH), 6.71 (d, *J* = 7.8 Hz, 2H, ArH), 6.53 (d, *J* = 7.2 Hz, 6H, ArH), 6.31 (d, *J* = 7.2 Hz, 4H, ArH), 6.20 (s, 2H, ArH), 5.89 (s, 4H, CH), 4.40 ~ 4.31 (m, 16H, OCH_2), 3.72 (s, 12H, OCH_3), 3.68 (s, 12H, OCH_3), 2.29, 2.22 (s, s, 12H, CH_3).

2j (R = CH_2CH_3, R′ = C_5H_{11}): white solid, Yield: 83%, mp: 90.3–91.8 °C. IR (KBr) υ: 2926(s), 2854(m), 1763(vs), 1737(s), 1505(m), 1442(m), 1380(w), 1306(m), 1202(s), 1126(m), 1084(m), 901(w), 850(w), 813(w), 716(w) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 6.65 (s, 1H,ArH), 6.62 (s, 2H, ArH), 6.59 (s, 1H, ArH), 6.22 (s, 12H, ArH), 4.59 (t, *J* = 7.8 Hz, 4H, CH), 4.29 ~ 6.26 (m, 16H, OCH_2), 3.75 (s, 16H, OCH_2), 1.80–1.86 (m, 12H, CH_2); 1.26 ~ 1.23 (m, 32H, CH_2), 0.85 (t, *J* = 7.2 Hz, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 14.1, 18.4, 22.7, 27.9, 28.1, 29.3, 29.8, 32.1, 34.5, 35.6, 51.9, 58.4, 60.9, 67.1, 100.7, 126.2, 126.5, 128.4, 128.6, 154.4, 169.3, 169.7, 170.1

2k (R = CH_2CH_3, R′ = C_6H_5): white solid, Yield: 80%, mp: 83.6–85.1 °C. IR (KBr) υ = 3058(w), 2925(w), 2377(w), 1758(vs), 1620(s), 1500(s), 1443(m), 1404(m), 1384(m), 1303(m), 1203(s), 1163(m), 1115(m), 1080(m), 1029(w), 925(w), 855(w), 811(w), 701(w). ^1H NMR ($CDCl_3$) δ: 7.03 (d, *J* = 7.8 Hz, 2H, ArH), 6.92 (s, 12H, ArH), 6.66 (s, 8H, ArH), 6.34 (s, 2H, ArH); 6.31(s, 2H, ArH), 6.24 (s, 2H, ArH), 5.94 (s, 4H, CH), 4.41 ~ 4.30 (m, 16H, OCH_2), 4.20 (q, *J* = 14.4 Hz, 8H, OCH_2), 4.15 (q, *J* = 14.4 Hz, 8H, OCH_2), 1.22 (m, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 14.1, 18.4, 35.3, 42.8, 51.9, 52.1, 58.4, 60.9, 61.1, 66.3, 67.1, 67.3, 99.3, 100.6, 125.5, 126.7, 127.5, 128.9, 132.2, 142.0, 154.5, 154.8, 168.8, 169.2.

2l (R = CH_2CH_3, R′ = $C_6H_4CH_3$-*p*): white solid, Yield: 75%, mp: 120.8–122.2 °C. IR (KBr) υ: 2983(w), 2922(w), 2316(w), 1760(vs), 1612(w), 1587(w), 1503(s), 1439(m), 1405(m), 1306(m), 1208(s), 1113(s), 1082(s), 1023(m), 925(w), 857(w), 812(w), 723(w) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 6.75 (d, *J* = 7.2 Hz, 10H, ArH), 6.55 (d, *J* = 6.6 Hz, 8H, ArH), 6.35 (d, 2H, ArH), 6.30 (s, 2H, ArH), 6.21 (s, 2H, ArH), 5.90 (s, 4H, CH), 4.35–4.39 (m, 12H, OCH_2), 4.27–4.25 (m, 4H, OCH_2), 4.20 (q, *J* = 7.2 Hz, 8H, OCH_2); 4.15 (q, *J* = 7.2 Hz, 8H, OCH_2), 2.22 (s, 12H, CH_3), 1.23 (m, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 14.1, 18.4, 21.1, 42.5, 51.8, 58.4, 60.9, 61.1, 67.0, 67.3, 99.6, 100.7, 126.8, 127.6, 128.3, 129.0, 132.2, 134.5, 139.0, 154.4, 154.8, 168.9, 169.2.

2m (R = CH_2CH_3, R′ = $C_6H_4NO_2$-*m*): light yellow solid, Yield: 82%, mp: 93.6–95.0 °C. IR (KBr) υ: 2985(w), 2854(w), 2345(w), 1758(vs), 1613(m), 1587(m), 1529(s), 1503(s), 1442(m), 1407(m), 1383(s), 1305(w), 1207(s), 1114(m), 1078(m), 921(w), 857(w), 808(w), 737(w) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.80 (d, *J* = 7.2 Hz, 4H, ArH), 7.29 (s, 2H, ArH), 7.11 (s, 8H, ArH), 6.48 (s, 2H, ArH), 6.31 (s, 2H, ArH), 6.29 (s, 2H, ArH), 6.01 (s, 4H, ArH), 5.22 (s, 2H, CH), 4.58 ~ 4.44 (m, 16H, OCH_2), 4.19 (d, *J* = 6.6 Hz, 8H, OCH_2), 4.14 (d, *J* = 6.6 Hz, 8H, OCH_2), 1.26–1.22 (m, 12H, CH_3), 0.90 (t, *J* = 7.2 Hz, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 14.1, 18.4, 42.6, 58.4, 61.2, 65.9, 66.3, 66.6, 99.3, 120.9, 123.6, 128.5, 130.9, 135.6, 144.7, 147.7, 154.8, 155.1. 168.3, 168.6.

Results and discussion

It has reported that $BF_3{\cdot}OEt_2$ can efficiently catalyzed cyclocondensation of 1,3-dialkoxybenzene or 3-alkoxyphenol with various aldehydes to form resorcinarene octaalkyl [9, 10] or tetraalkyl [24, 25] ethers. We reasoned that 1,3-(dialkoxycarbonylmethoxy)benzene, which are very similar to 1,3-dialkoxybenzene in structure, would smoothly undergo this kind condensation reaction with aldehydes to directly form resorcinarene derivatives with eight functional acetates, which are key intermediates for the chemical modification of resorcinarene [24–26]. 1,3-(Dialkoxycarbonylmethoxy)benzenes (R = CH_3, C_2H_5) **1a–1b**, the starting materials for this work, were conveniently synthesized in very satisfied yields from a alkylation of resorcinol with methyl or ethyl α-chloroacetates in the refluxing system of K_2CO_3/KI/acetone for about 10 h. Then the cyclocondensation of **1a–1b** with aldehydes were carried out in CH_2Cl_2 in the presence of $BF_3{\cdot}Et_2O$ as Lewis acid catalyst at room temperature for overnight. After workup we are very satisfied to find that the resorcinarene *O*-acetates **2a–2m** were efficiently in good to excellent yields (Table 1). Various aliphatic aldehydes with two to nine carbon chains and aromatic aldehydes with electron-donating or withdrawing substituent could be employed in the reaction but had not much influence on the yield of resorcinarene. Even *m*-nitrobenzaldehyde can give very high yield of resorcinarene *O*-acetate **2m**. It is reported that in the acid-catalyzed reaction nitrobenzaldehyde could not react with resorcinol to form tetranitrophenyl resorcinarene and the reaction was only stopped at dimerization step [2]. This result demonstrated that this reaction has great

Table 1 Data of the synthesis of resorcinarene *O*-acetates

Entry	R	R′	Compd	Yield (%)
1	CH_3	CH_2CH_3	**2a**	69
2	CH_3	$(CH_2)_2CH_3$	**2b**	63
3	CH_3	$(CH_2)_4CH_3$	**2c**	67
4	CH_3	$(CH_2)_5CH_3$	**2d**	57
5	CH_3	$(CH_2)_6CH_3$	**2e**	72
6	CH_3	$(CH_2)_7CH_3$	**2f**	62
7	CH_3	$(CH_2)_8CH_3$	**2g**	67
8	CH_3	Ph	**2h**	76
9	CH_3	*p*-$CH_3C_6H_4$	**2i**	56
10	CH_2CH_3	$(CH_2)_4CH_3$	**2j**	83
11	CH_2CH_3	C_6H_5	**2k**	80
11	CH_2CH_3	*p*-$CH_3C_6H_5$	**2l**	75
12	CH_2CH_3	*m*-$NO_2C_6H_4$	**2m**	82

generality and can be used for the preparation of resorcinarene *O*-acetates with versatile substituents (Scheme 1).

The structures of all prepared resorcinarene derivatives **2a–2m** were fully characterized by ^{1}H and ^{13}C NMR, MS, and IR spectra. As for example in ^{1}H NMR spectrum of **2c** (Fig. 1) the –OCH_2CO– groups show slightly broad peak at about 4.28 ppm and the methoxyl groups displays a singlet at 3.76 ppm, which shows the eight –$OCH_2CO_2CH_3$ are in nearly same environments. The proton sign of four bridging methyne appears a singlet at 4.58 ppm and the protons at C-2 and C-5 position of resorcinol ring show two single peaks in 1:1 ratio at 6.61 and 6.21 ppm and the four pentyl groups display three signs at 1.85 ppm for methylene groups ($\underline{CH_2}CH_2CH_2CH_2CH_3$), 1.29 ppm for propylene units ($CH_2\underline{CH_2CH_2CH_2}CH_3$) and 0.85 ppm for methyl groups clearly shows that the four resorcinol rings and four pentyl groups are in same environments and the whole molecule is in *rccc* (all *cis*) configuration [2, 13, 14]. The ^{1}H NMR spectra of other resorcinarenes with alkyl bridging groups show similar peak pattern and we could get the results that all of them adopt *rccc* (all *cis*) configuration. The resorcinarenes with aryl bridging groups show a little complicated ^{1}H NMR spectra situation, from which we can not assigned the exact configuration of the molecules.

The X-ray single crystal analysis of four representative compounds **2c**, **2h**, **2i** and **2m** unambiguously confirms the structures of resorcinarenes. The crystal data and refinement details are given in Table 2 and the molecular structures are showed in Figs. 2, 3, 4 and 5. From Fig. 2 it can be seen that the four bridging pentyl groups stretch to lower rim of resorcinarene and eight *O*-acetate groups

Scheme 1 The catalyzed synthesis of resorcinarene *O*-acetates

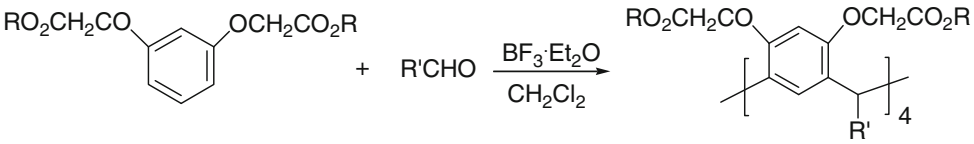
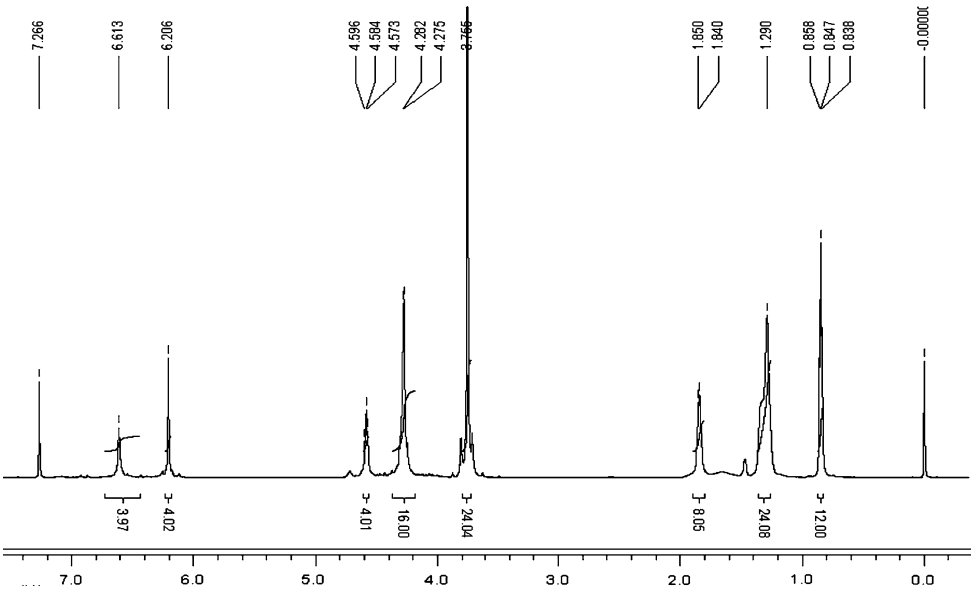


Fig. 1 The ^{1}H NMR spectra of resorcinarene *O*-acetate 3c



are located at upper rim. All four resorcinol rings stretch to upper direction, two of which are almost vertical, and the other two nearly horizontal. So the molecule is in an *rccc* (all *cis*) configuration, which also supports the ^{1}H NMR analysis. Form Fig. 3 it is interesting to find that phenyl resorcinarene **2h** is in *rctt* (*cis–trans–trans*) configuration, which is similar to the single crystal structure of the ethyl resorcinarylacetates [22] and The four resorcinol units in the ring were divided into two groups with two resorcinol units at almost perpendicular direction and other two resorcinol rings nearly in horizontal position. The stretching direction of two perpendicular resorcinol rings is opposite. One is upper standing and the other is upside down. The four phenyl groups are also divided into two groups with two neighboring phenyl groups at locating in upper direction, while other two phenyl groups stretching to down direction. The molecule **2i** and **2m** (Figs. 4, 5) are also in *rctt* (*cis–trans–trans)* configurations. The *rccc* (all *cis*) configuration and *rctt* (*cis–trans–trans*) configuration are two main existing configurations of resorcinarenes [7, 27, 28]. From above crystal data we might tentatively conclude that alkyl resorcinarenes prefer *rccc* configuration, while aryl resorcinarenes usually adopt *rctt* configuration.

Table 2 Crystal data and structure refinement details of compounds

Phase	2C	2h	2i	2m
Molecular formula	$C_{72}H_{96}O_{24}$	$C_{76}H_{72}O_{24}$	$C_{80}H_{76}O_{24}$	$C_{84}H_{84}N_4O_{32}$
Formula weight	1,345.49	1,369.34	1,421.41	1,661.56
T/K	296(2)	296(2)	296(2)	273(2)
Wavelength/nm	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	P 21/c	P-1	P-1	P
a/nm	20.894(6)	11.4930(15)	11.5414(18)	11.2418(12)
b/nm	20.229(5)	12.2750(16)	11.8030(18)	24.785(3)
c/nm	18.726(5)	14.632(3)	14.520(2)	15.2999(16)
α (°)	90	107.238(2)	73.899(2)	90.00
β (°)	90	99.818(2)	84.366(2)	103.931(2)
γ (°)	90	113.899(2)	82.272(2)	90.00
V (nm^3)	7,915(4)	1,699.7(5)	1,879.3(5)	4,137.5(8)
Z, calculated density (mg cm^{-3})	4, 1.129	1, 1.338	1, 1.256	4, 1.334
F(000)	2,880	720	748	1,744
Absorption coefficient (mm^{-1})	0.084	0.100	0.093	0.103
θ range/(°)	1.40–25.01	1.55–25.01	1.81–25.00	2.03–25.00
Limiting indices	$-24 \le h \le 24$, $-23 \le k \le 24$, $-22 \le l \le 22$	$-13 \le h \le 13$, $-14 \le k \le 14$, $-16 \le l \le 17$	$-13 \le h \le 13$, $-14 \le k \le 12$, $-17 \le l \le 17$	$-13 \le h \le 12$, $-29 \le k \le 28$, $-18 \le l \le 18$
Reflections collected/unique	57,036/13,965 [R(int) = 0.1684]	12,386/5,955 [R(int) = 0.0254]	13,716/6,564 [R(int) = 0.0510]	21,348/7,228 [R(int) = 0.0643]
Completeness to theta	99.9%	99.3%	99.4%	99.1%
Data/restraints/parameters	13,965/1,230/968	5,955/0/454	6,564/7/475	7,228/13/536
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R indices[$I > 2\sigma(I)$]	$R_1 = 0.1209$, $wR_2 = 0.2883$	$R_1 = 0.1017$, $wR_2 = 0.3261$	$R_1 = 0.0904$, $wR_2 = 0.2553$	$R_1 = 0.1095$, $wR_2 = 0.2830$
R indices (all data)	$R_1 = 0.3145$, $wR_2 = 0.3728$	$R_1 = 0.1377$, $wR_2 = 0.3615$	$R_1 = 0.1768$, $wR_2 = 0.3245$	$R_1 = 0.2228$, $wR_2 = 0.3335$
Goodness-of-fit on F^2	1.066	1.175	1.082	1.003
Largest diff. peak and hole/(e · nm^{-3} × 10^{-3})	0.591 and −0.512	1.001and −0.694	0.867 and −0.928	0.705 and −0.504

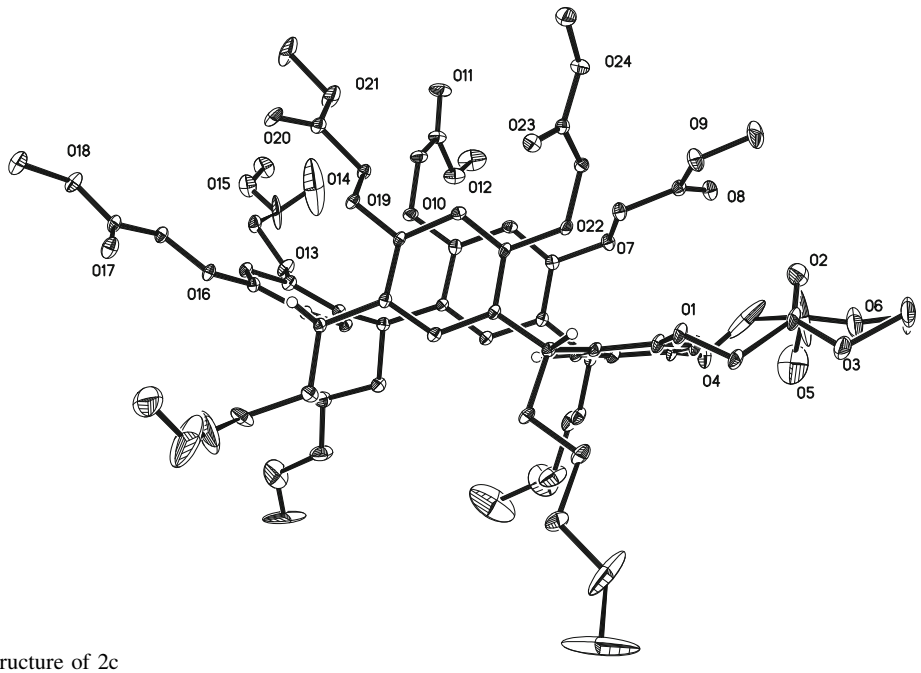


Fig. 2 The crystal structure of 2c

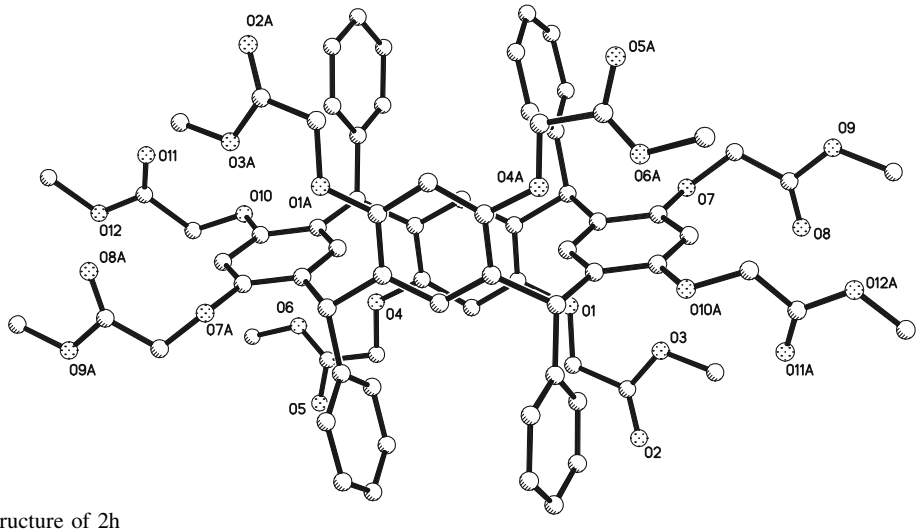


Fig. 3 The crystal structure of 2h

In summary the results reported here established an alternate efficient route to prepare a wide range of resorcinarene *O*-acetates in high yields, which are the key intermediates in the chemical modification process of resorcinarenes. The reaction procedure is convenient, involving simple experimental procedure and product isolation, thus dispense with extensive recrystallisation or chromatographic purification steps. This present protocol could be used for the convenient synthesis of a number of functionalized resorcinarenes.

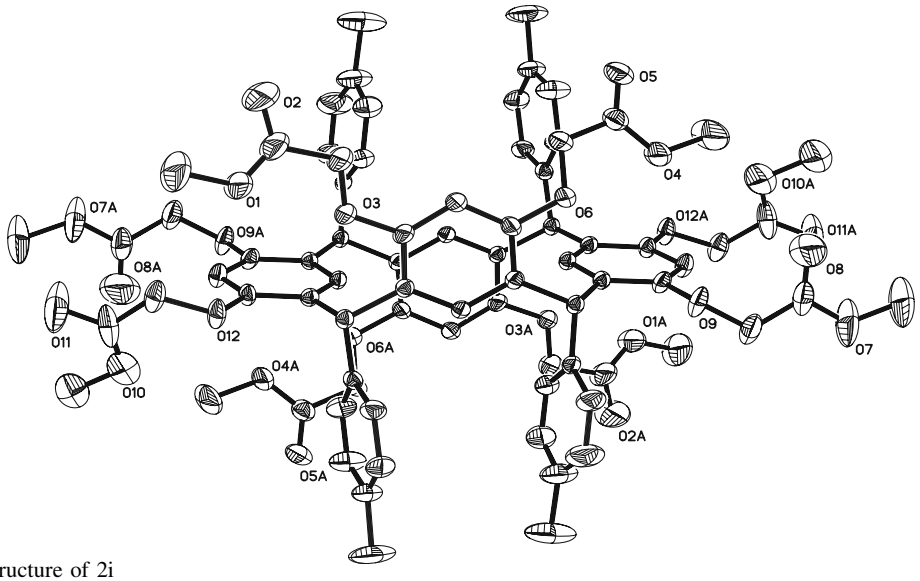


Fig. 4 The crystal structure of 2i

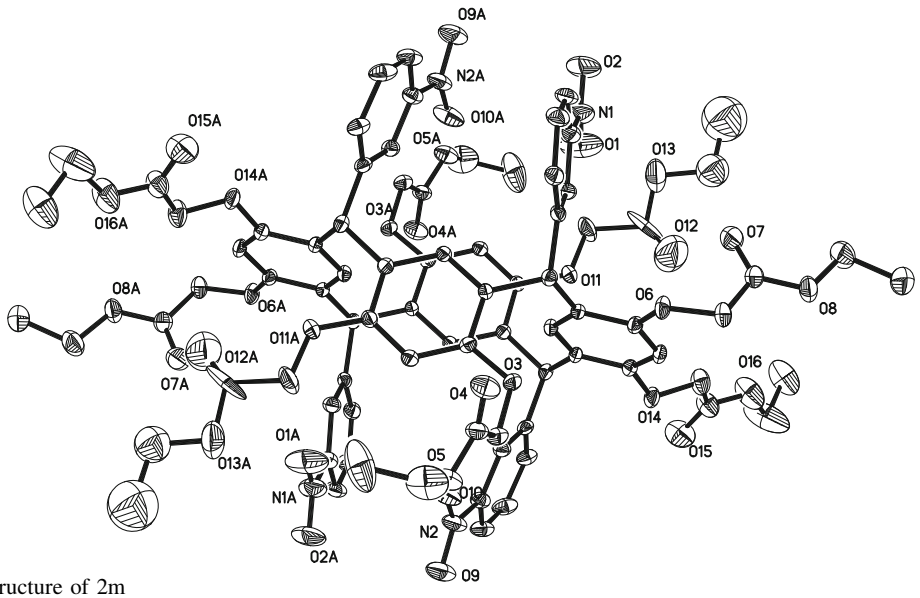


Fig. 5 The crystal structure of 2m

Supplementary material

Single crystal X-ray diffraction data are deposited with CCDC (Deposition numbers **2c**: 733522; **2h**: 725255; **2i**: 725256; **2m**: 753141).

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