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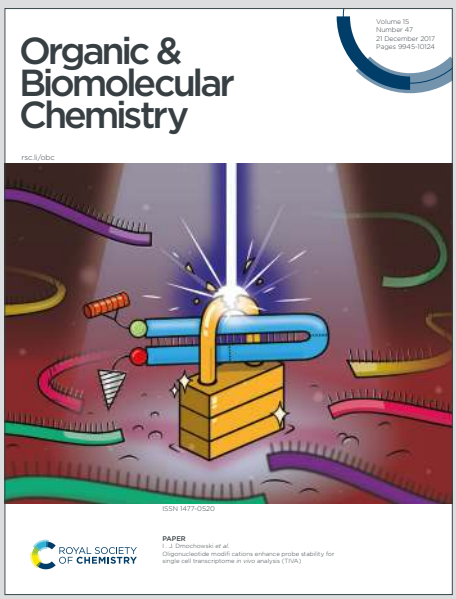

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ARTICLE

Synthesis and application of 3,4,7,8-*tetrakis*-*exo*-methylenecycloocta-1,5-diene as a versatile Diels-Alder diene. Synthesis of V-shaped cyclooctatetraene fused acenes

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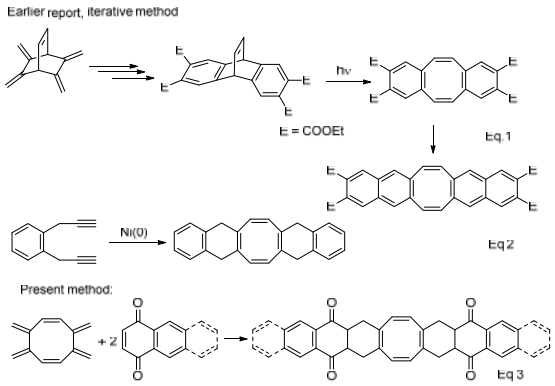
V-Shaped molecules with cyclooctatetraene (COT) core and rigid acene wings are an interesting class of compounds from the point of view of synthetic challenge and their applications in various fields such as photonics and molecular electronics. A new Diels-Alder diene, namely 3,4,7,8-*Tetrakis*-*exo*-methylenecycloocta-1,5-diene (**1**) has been synthesized in multi-gram scale by the debromination of 1,4,5,8-tetrakis-bromomethylcycloocta-1,3,5,7-tetraene (**2**) using either zinc powder or NaI. Compound **1** was used as a Diels-Alder diene with various dienophiles to yield the corresponding double Diels-Alder adducts. The Diels-Alder adducts have COT core and dihydroaromatic wings which were aromatized with a variety of reagents. The methodology described herein provides a direct and shorter route for the synthesis of COT fused with rigid aromatic wings (V-shaped) compared to the existing iterative multistep synthesis of such compounds.

Introduction

Cyclooctatetraene (COT) is a classic example of flexible π-system.[1] It undergoes ring inversion as well as double bond shifting isomerization.[2] COT has served as a simple starting material for the synthesis of complex organic molecules.[3] Molecules having flexible COT moiety at the centre and flat rigid π-systems as wings have been shown to exhibit environment sensitive dual fluorescence due to V-shape-planar conformational dynamics.[4] V-Shaped molecules with COT core and acene wings are potentially useful in photonics and molecular electronics.[4,5] In the literature such V-shaped molecules have been synthesized in an iterative manner building the rigid aromatic units one at a time.[6] Moreover the central COT unit is obtained by the photochemical isomerization of bicyclo[2.2.2]octatriene moiety (Scheme 1, eq.1). Nickel catalysed intermolecular [2+2+2+2] cycloaddition to construct COT ring is another important strategy developed originally by Reppe[7] and more recently by Wender[8] for arene fused COT derivatives (Scheme 1, eq.2). Nickel catalysed [2+2+2+2] cycloaddition of propargyl alcohol for the synthesis of 1,4,5,8-tetrakis-hydroxymethylcycloocta-1,3,5,7-tetraene has been reported by Streitweiser.[9] Representative examples of tetrakis-exomethylene (**A,**[10] **B,**[11] **C**[12] and **D**[13]) compounds used as building blocks in Diels-Alder reactions reported in the literature are shown in Figure 1. Although synthesis of **E**[14] and



Scheme 1 Synthesis of V-shaped molecules with COT core.

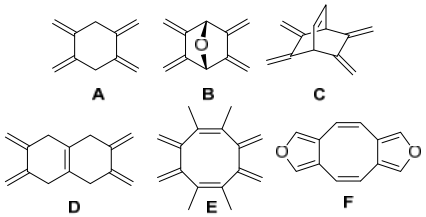


Figure 1 Selected examples of tetrakis-exomethylene building blocks.

F[15] is reported, their utilization as building block in cycloaddition reactions has not been fully explored. Herein we describe multi-gram scale synthesis of a new and useful bis-diene, namely 3,4,7,8-*tetrakis*-*exo*-methylenecycloocta-1,5-diene (**1**) and its use as a double Diels-Alder diene (Scheme 1 eq.3). A variety of dienophiles underwent Diels-Alder reaction with **1** including

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Electronic Supplementary Information (ESI) available: [1H and 13C NMR spectra of products, CCDC 2017969 (**4a**), 2017970 (**14c**), 2017972 (**13b**) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Center.]. See DOI: 10.1039/x0xx00000x

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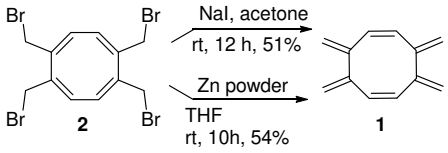
quinones that afforded the corresponding dihydroaromatic derivatives which are fully aromatized by a variety of methods.

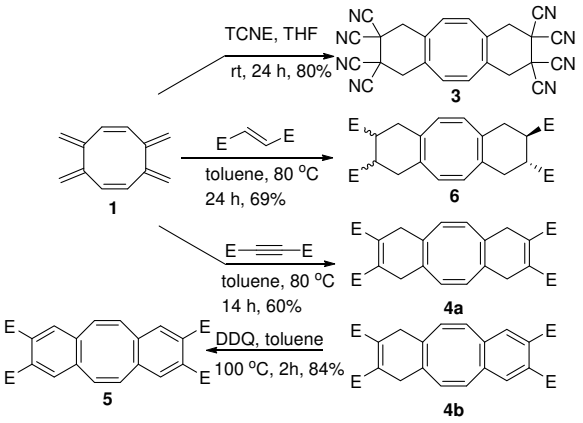
Results and discussion

1,4,5,8-Tetrakis-bromomethylcycloocta-1,3,5,7-tetraene (**2**) was prepared on gram scale from the corresponding tetra alcohol which in turn was prepared by the procedure of Streitweiser[9] by the [2+2+2+2] cycloaddition of propargyl alcohol. Compound **2** is a stable colorless solid and can be stored at room temperature for several months. Debromination of 1,4,5,8-tetrakis-bromomethylcycloocta-1,3,5,7-tetraene (**2**) was carried out by two methods (Scheme 2). In the first method **2** was refluxed in acetone in the presence of excess NaI to afford **1** in 50% yield.[16] In another method **2** was treated with 5-fold excess Zn powder in THF at room temperature to afford **1** in 54% yield (scheme 2)[17].



Scheme 2 Synthesis of bis-diene (**1**) from tetrabromide (**2**)

In the Zn powder method simple filtration of Zn residues at the end of the reaction gave THF solution of **1** in pure state. When carried out in gram scale the exothermic nature of this reaction could be observed leading to gentle boiling of THF. Due to operational simplicity the Zn powder method was used for all further reactions. The ^{1}H NMR spectrum of **1** exhibited three singlets one corresponding to the ring protons (6.10 ppm, singlet) and one corresponding of each of the exo-methylene protons (5.13 ppm, singlet and 4.90 ppm, singlet). Compound **1** in pure state is a colorless liquid and unstable at room temperature in air leading to the formation of insoluble white solid presumably due to polymerization. However, in solution (in THF or toluene) it is quite stable for several days. The crude product obtained from the Zn powder reaction in THF solution was pure (by ^{1}H NMR) and it was used as such for further reactions. Addition of tetracyanoethylene (TCNE) was carried out in THF solution of **1** at room temperature for 24 h to yield the bis-adduct (**3**) in 80% yield as a colorless solid (Scheme 3). The crude product was washed with CH_2Cl_2 to remove excess unreacted TCNE. ^{1}H NMR spectrum showed a singlet at 5.90 ppm for the COT ring protons and an AB quartet at 3.47 and 3.20 ppm (J_{AB} = 17.6 Hz) for the methylene protons. Addition of diethyl acetylenedicarboxylate to **1** was carried out in toluene at 80 ^{o}C for 14 h. The bis-adduct (**4a**) was obtained in 60% yield as a colorless solid along with trace amounts of partially dehydrogenated derivative **4b** (see ESI). After column chromatographic purification pure product **4a** was obtained as colourless crystalline solid. Structure of **4a** was unequivocally confirmed by spectroscopic data and single crystal XRD data (Figure 2). The mixture of adducts (**4a** and **4b)** was further treated with DDQ in toluene to yield compound **5** as a colorless solid in 84 % yield (Scheme 3). Similarly, addition of diethyl fumarate to **1** yielded the bis-adduct in 69% yield as a single



diastereomers (**6**) as evident form the ^{1}H NMR spectrum of the

Scheme 3 Diels-Alder reactions of **1** with various dienophiles. (E = $COOC_2H_5$)

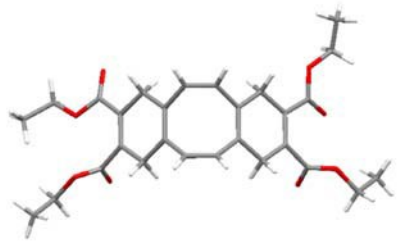
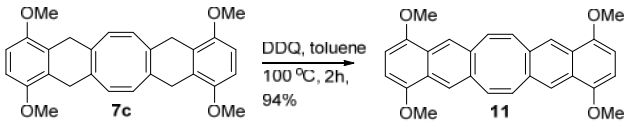
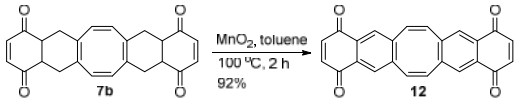


Figure 2 Structure of **4a** according to single crystal XRD data



Scheme 5 Dehydrogenation of **7c** to **11** using DDQ

crude product. The stereochemistry is tentatively assigned as *trans-anti-trans* isomer. Cycloaddition of bis-diene **1** to a variety of quinones was carried out in THF. Benzoquinone (**7a**) reacted at room temperature to give the corresponding bis-adduct (**7b**) as a white solid that was completely insoluble in all the common organic solvents including DMSO (Scheme 4). However, ESI-MS showed molecular ion peak at m/z 372.1431 corresponding to the bis-adduct (**7b**). The bis-adduct (**7b**) when treated with dimethyl sulfate and K_2CO_3 in acetone yielded a soluble tetramethoxy derivative (**7c**) which was thoroughly characterized by spectroscopic methods (Scheme 4). Similarly, quinones (**8a-10a**) reacted with **1** to yield the corresponding bis-adducts (**8b**-**10b**) as insoluble solids. Treatment of the insoluble adducts **8b**-**10b** with dimethyl sulfate and K_2CO_3 gave the



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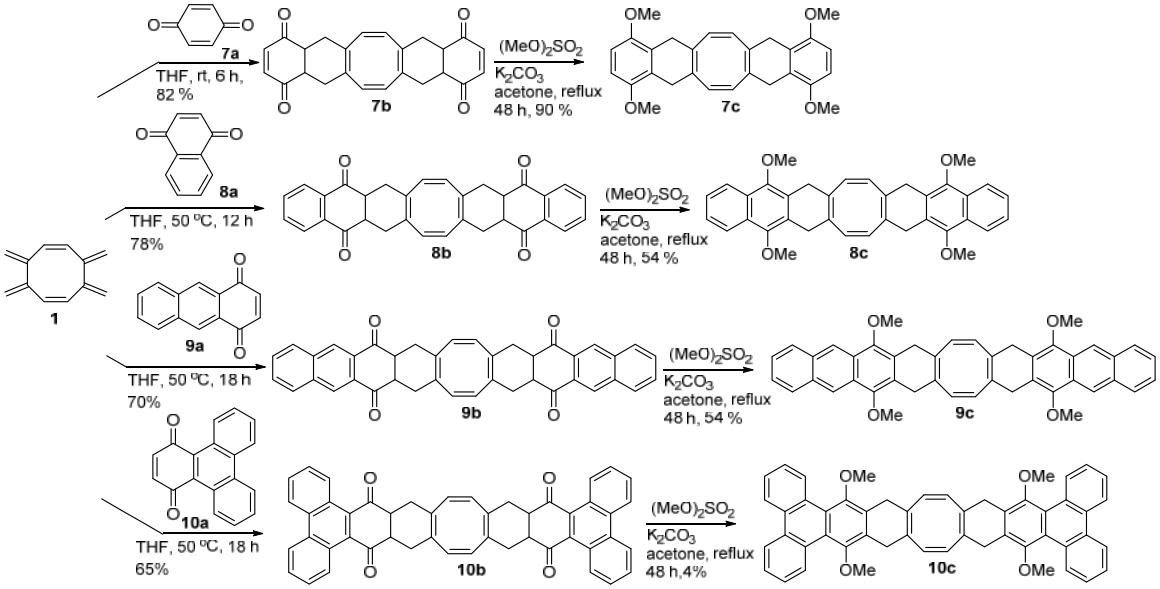
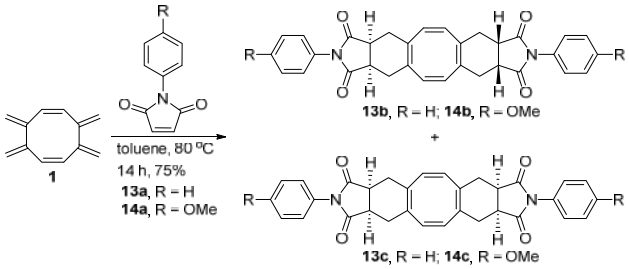
Scheme 6 Oxidation of **7b** to quinone **12** using MnO_2



Scheme 4 Diels-Alder reaction of **1** with various quinones and conversion of the insoluble bis-adducts to soluble tetramethoxy derivatives.

corresponding tetramethoxy derivatives (**8c**-**10c**). Adducts **8b**-**10b** were characterized by IR spectroscopy and ESI-MS spectrometry and the tetramethoxy derivatives **8c**-**10c** were thoroughly characterized by various spectroscopic methods. The tetramethoxy derivative **7c** was further aromatized by dehydrogenation using DDQ to **11** in excellent yields (Scheme 5). The bis-adduct **7b** was further oxidized to the corresponding quinone **12** using MnO_2 in toluene in 92% yield (Scheme 6).

Cycloaddition of N-aryl-maleimide derivatives **13a** and **14a** to **1** proceeded smoothly in toluene to give the bis-adduct in nearly 1:1 ratio of mixture of diastereomers (Scheme 7). The diastereoisomers were separated by repeated column



Scheme 7 Diels-Alder reaction of **1** with N-arylmaleimides

chromatography on silica gel (eluant hexane/ethyl acetate (10:3 v/v) and the pure diastereoisomers thus obtained were thoroughly characterized by spectroscopic methods. Assignment of relative stereochemistry of the two isomers is based on symmetry of the structure of the diastereoisomers.

The geometry of **13c** and **14c** (cis-syn-cis isomer) is more symmetrical ("W" shaped) and hence the protons on the COT ring appeared as a singlet because of chemical shift

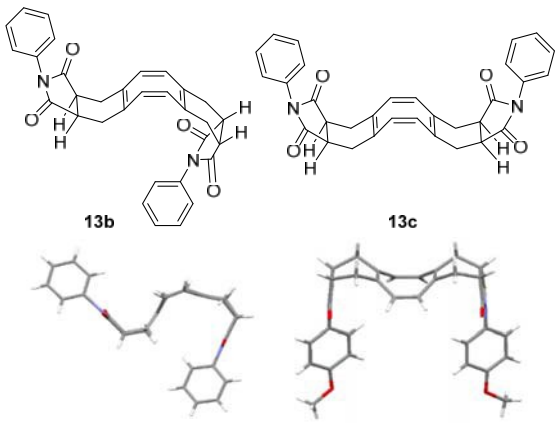


Figure 3. Geometries of **13b** (top left) and **13c** (top right). Structure of **13b** (bottom left) and **14c** (bottom right) in the crystal according to single crystal XRD data

equivalence. The methoxy protons of **14c** appeared as one singlet of 6H intensity. On the other hand geometry of isomers **13b** and **14b** (cis-anti-cis isomer) is "S" shaped and less symmetrical. Therefore, the protons of the COT ring appeared as an AB quartet. The methoxy protons of **14b** also appeared as two singlets of each 3H intensity due to chemical shift non-equivalence of the methoxy groups. The structure and stereochemistry of **13b** and **14c** were also confirmed unambiguously by single crystal XRD data which clearly revealed the stereochemistry and geometry of these two isomers (Figure 3).

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Conclusion

Bis-diene **1** was synthesized by the debromination of tetra-bromide **2** and this reaction was carried out in grams scale. The bis-diene (**1**) thus obtained was tested for its viability to undergo double Diels-Alder cycloaddition reaction with a variety of dienophiles. Bis-cycloadducts obtained from **1** and several quinones were insoluble in all the common organic solvents. After confirming the formation of the bis-adducts through mass spectrometry they were converted into tetramethoxy substituted benzenoid derivatives by reacting with dimethyl sulfate and K_2CO_3 in refluxing acetone. The tetramethoxy derivatives were soluble in common organic solvents were characterized by various spectroscopic methods. The tetramethoxy derivatives were converted into fully aromatic acenes by treatment with DDQ. The Diels-Alder adducts were converted into the corresponding quinonoide derivatives by treatment with MnO_2. Bis-diene **1** is a very useful building block and provides an easy access to V-shaped molecules with wings consisting of planar polycyclic arenes with COT at the center.

Experimental section

Tetrabromide **2** was synthesized by treatment of the tetra alcohol with PBr_3. A solution of phosphorus tribromide (4.2 mL, 44.6 mol) in dichloromethane (50 mL) was added dropwise to a suspension of the corresponding tetra alcohol (2 g, 8.9 mol) in dichloromethane (50 mL) at room temperature over period of 60 minutes. The reaction mixture was stirred for 5 h, diluted with CH_2Cl_2 (50 mL), washed sequentially with water, saturated $NaHCO_3$ solution, brine and then dried over anhydrous $NaSO_4$. The solvent was evaporated and residue was purified by chromatography on silica gel (elution: hexane/ethyl acetate, 50:1 v/v) to afford **2** as white solid (3.8 g, 90%); mp 91 ˚C;[9] IR (KBr, cm^{-1}): ν 2960, 1639, 1423, 1048, 848, 608; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (s, 4H), 4.13 (d, *J* = 10.8 Hz, 4H), 3.99 (d, *J* = 10.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 138.7, 131.9, 33.7; HRMS (ESI, m/z) calc for $C_{12}H_{13}Br_4$ 472.7751(M+H), found 472.7756

Bis-diene 1 was synthesized by the following methods.

Method A: Under N_2 atmosphere 10 mL of acetone was added to an oven dried two neck RB flask fitted with a rubber septum containing **2** (475 mg, 1mmol) and sodium iodide (900 mg, 6 mmol). The mixture was stirred at room temperature for 10 h after which the mixture was diluted with 20 mL of dichloromethane and the organic layer was extracted with saturated sodium thiosulfate solution. The organic layer was dried over anhydrous Na_2SO_4 and then solvent was removed using a rotavapor. The crude product was subjected to column chromatography (eluant hexane) to afford compound **1** as colourless gel (80mg, 51%).

Method B: Under N_2 atmosphere 50 mL of THF was added to an oven dried two neck RB fitted with a septum containing **2** (5 g, 10.5 mmol) and solution was stirred for 10 minutes. Excess zinc powder (5 g, 77 mmol) added in several portions and the reaction mixture was stirred at room temperature for 10h. It was filtered through a short pad of celite and solvent was removed using a rotavapor. The crude product was purified by column chromatography (eluant hexane) to afford compound **1** as colourless gel (886mg, 54%);; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10 (s, 4H), 5.12(s, 4H), 4.90 (s, 4H); ^{13}C NMR (100 Hz $CDCl_3$): 146.9, 130.3, 116.59 ; HRMS (ESI, m/z) calculated for $C_{12}H_{12}$: 156.0931. Found 156.0939.

Compound **3**: A solution of tetracyanoethylene (128 mg, 2 mmol) and **1** [prepared from **2** (238 mg, 0.5 mmol)] in THF (5 mL) was stirred at room temperature for 20 h. The solvent was evaporated using a rotavapour and residue was washed with CH_2Cl_2 to afford **3** as white solid (82 mg, 80%); IR (KBr, cm^{-1}): ν ; ^{1}H NMR (400 MHz, DMSO-d_6): 5.90 (s, 4H), 3.47 (d, J = 17.6 Hz, 4H), 3.20 (d, J = 18Hz, 4H); ^{13}C NMR (100 Hz DMSO-d6):132.8, 127.9, 111.8, 111.7, 38.8, 33.6; HRMS (ESI, negative ion mode, m/z) calc for $C_{24}H_{11}N_8$ (M-H)$^-$ 411.1109., found 411.1117.

Compound **4a**: A solution of diethyl acetylenedicarboxylate (170 mg, 2 mmol) and **1** [prepared from **2** (238 mg, 0.5 mmol)] in toluene (5 mL) was heated at 80 ˚C for 14 h. The solvent was evaporated and residue was purified by chromatography on silica gel (eluant hexane/ ethyl acetate, 20:1 v/v) to afford **4a** as white solid (75 mg, 60%); compound **4a** mp 91 ˚C; IR (KBr, cm^{-1}): ν 2988,1726, 1290, 1066; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (s, 4H), 4.22 (q, *J* = 8Hz, 8H), 2.92 (m, 8H), 1.29 (t, *J* = 8Hz, 12H); ^{13}C NMR (100 Hz $CDCl_3$): 167.7 , 132.7, 132.0, 129.4, 61.3, 32.6, 14.1; HRMS (ESI, m/z) calc for $C_{28}H_{28}O_8$ Na: 515.1682 Found 515.1682**.**

Compound **4b:** ^{1}H NMR (400 MHz, $CDCl_3$) 7.34 (s, 2H), 6.50(d, J= 11.6 Hz, 2H), 6.02 (d, J= 11.6 Hz, 2H), 4.33(q, J= 7.2Hz, 4H), 4.22 (q, J= 7.2Hz, 4H), 2.9 (m, 4H), 1.34 (t, J= 7.2Hz, 6H), 1.29 (t, J= 7.2Hz, 6H); [methylene and ester protons on unaromatized six membered ring have merged with major compound **4a** protons]; ^{13}C NMR (100 Hz $CDCl_3$): 167.69, 167.4, 140.8, 135.2, 131.8, 130.8, 130.6, 129.8, 128.8, 61.7, 61.3, 32.1, 14.2, 14.1: HRMS (ESI, m/z) calc for $C_{28}H_{30}O_8$ (M+H): 494.1938. Found 495.1984.

Compound **6**: A solution of diethyl fumarate (172 mg, 2 mmol) and **1** [prepared from **2** (238 mg, 0.5 mmol)] in toluene (5 mL) was heated at 80 ˚C for 24 h. Solvent was removed using a rotavapour and brown gel obtained was purified by column chromatography to afford compound **6** as a white solid (87 mg, 69%); mp 90 ˚C; IR (KBr, cm^{-1}): ν 2980, 1731, 1457, 1369, 1315, 1255, 1176, 1048; ^{1}H NMR (400 MHz, $CDCl_3$): 5.66 (d, *J*= 12.8 Hz, 2H), 5.61 (d *J* = 12 Hz, 2H), 4.14 (m, 8H), 3.1 (m, 2H), 2.72 (m, 2H), 2.27 (m, 4H), 2.14 (m, 4H), 1.25 (m, 12H); ^{13}C NMR (100 Hz $CDCl_3$): 174.6, 174.5, 133.0, 132.9, 132.4, 132.3, 132.2, 131.79, 131.72, 131.1, 125.2, 60.84, 45.9, 41.6, 41.5, 32.6, 32.38, 32.34, 14.3; HRMS (ESI, m/z) calc for $C_{28}H_{37}O_8$ (M+H)$^+$: 501.2483 Found 501.2477;

Compound **5**: To a solution of **4a** (49.6mg, 0.1mmol) in 5ml of toluene was added DDQ (46.5mg, 0.21mmol). The reaction mixture was heated at 100 °C for 8h and allowed to cool to room

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temperature, extracted with saturated sodium bicarbonate solution and chloroform. Organic layer was dried over anhydrous sodium sulphate, evaporated using a rotavapour and purified by column chromatography to afford **12** as white solid (41mg, 84%); mp 98˚C IR (KBr, cm^{-1}): ν 2980, 1715, 1560, 1285, 1056; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 4H), 6.80 (s, 4H), 4.30 (q, *J* = 7.2Hz, 8H), 1.32 (t, *J* = 7.2Hz, 12H), ^{13}C NMR (100 Hz $CDCl_3$): 167.1, 139.4, 133.4, 130.9, 129.8, 61.7, 14.1; HRMS (ESI, m/z) calc for $C_{28}H_{28}O_8Na$: 515.1682. Found 515.1682.

Compound **7b**: A solution of **1** [prepared from **2** (238 mg, 0.5 mmol)] and *p*-benzoquinone (108 mg, 2 mmol) in THF (10 mL) was stirred at room temperature for 6 h. The precipitate was filtered and was washed with CH_2Cl_2 to afford **7b** as an insoluble white solid (76 mg, 82%); IR (KBr cm^{-1}): ν 2988, 1726, 1290, 1066 cm^{-1}; HRMS (ESI, m/z) calc for $C_{24}H_{21}O_4$ $(M+H)^+$: 372.1434. Found 372.1431.

Compound **7c**: To the suspension of benzoquinone adduct (7b) (100 mg, 0.26mmol) in acetone (10 mL) dimethyl sulphate (197 mg, 1.56 mmol) and potassium carbonate (360 mg, 2.6 mmol) were added under N_2 atmosphere. The reaction mixture was refluxed for 48 h, cooled to room temperature and extracted with chloroform and water. Organic layer was dried over anhydrous Na_2SO_4 and concentrated using a rotavapour. The crude product was purified by column chromatography to afford compound **7c** as white solid (104 mg, 90%); mp 262 ˚C; IR (KBr, cm^{-1}): ν 2943, 2828 , 1474, 1434, 1251, 1093; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.61 (s, 4H), 5.88 (s, 4H), 3.76 (s, 12H), 3.21 (m,8H); ^{13}C NMR (100 Hz $CDCl_3$): 150.8, 133.2, 130.6, 124.28, 107.12, 55.78, 29.61; HRMS (ESI, m/z) calc for $C_{28}H_{29}O_4$ $(M+H)^+$: 429.2060. Found 429.2062.

Compound **8b**: A solution of **1** [prepared from **2** (238 mg, 0.5 mmol)] and 1,4-naphthoquinone (158 mg, 2 mmol) in THF (10 mL) was heated at 50 ˚C for 12 h. The precipitate obtained was filtered and was washed with CH_2Cl_2 to afford **8b** as an insoluble white solid (92 mg, 78 %); IR (KBr cm^{-1}); ν 2359, 2335, 1690,15921284, 1248; HRMS (ESI, m/z) calc for $C_{32}H_{24}O_4$ Na $(M+Na)^+$: 495.1572. Found 495.1563

Compound **8c**: To the suspension of **8b** (100 mg, 0.21 mmol) in acetone (10 mL) dimethyl sulphate (160 mg, 1.26 mmol) and potassium carbonate (292 mg, 2.1 mmol) were added under N_2 atmosphere. The reaction mixture was refluxed for 48 h, cooled to room temperature and extracted with chloroform and water. Organic layer was dried over anhydrous sodium sulphate and concentrated using a rotavapour. The crude product was purified by column chromatography to afford compound **8c** as a white solid (60 mg, 54%); mp 270 ˚C; IR (KBr, cm^{-1}): ν 2983, 2832 , 1596, , 1260, 1062 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (m, 4H), 7.44 (m, 4H), 5.99 (s, 4H), 3.9 (s, 12H), 3.60 (d, *J* =18.4 Hz, 4H), 3.47(d, *J* =18.4 Hz, 4H); ^{13}C NMR (100 Hz $CDCl_3$): 148.7, 133.4, 131.6, 127.3, 125.5, 124.9, 122.1, 61.3, 29.85; HRMS (ESI, m/z) calc for $C_{36}H_{32}O_4K$ $(M+K)^+$: 567.1938. Found 567.1939.

Compound **9b**: A solution of **1** [prepared from **2** (238 mg, 0.5 mmol)] and 1,4-anthraquinone (208 mg, 2 mmol) in THF (10 mL) was heated at 50 ˚C for 18 h. The precipitate was filtered and was washed with CH_2Cl_2 to afford **9b** as an insoluble white solid (100 mg, 70 %); IR (KBr cm^{-1}); ν 2359, 2338, 1693,1619,1585, 1261, 1251; HRMS (ESI, m/z) calc for $C_{40}H_{29}O_4(M+H)^+$: 573.206. Found 573.205.

Compound **9c:** To the suspension of compound **9b** (100 mg, 0.21 mmol) in acetone (10 mL) dimethyl sulphate (160 mg, 1.26 mmol) and potassium carbonate (292 mg, 2.1 mmol) were added under N_2 atmosphere. The reaction mixture was refluxed for 48h, cooled to room temperature and extracted with chloroform and water. The organic layer was dried over anhydrous sodium sulphate and then concentrated using a rotavapour. The crude product was purified by column chromatography to afford compound **9c** as white solid (60 mg, 54%), mp 270 ˚C; IR (KBr, cm^{-1}): ν 2983, 2832 , 1596, , 1260, 1062 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (m, 4H), 7.44 (m, 4H), 5.99 (s, 4H), 3.9 (s, 12H), 3.60 (d, *J*=18.4Hz, 4H), 3.47(d, *J*=18.4Hz, 4H); ^{13}C NMR (100 Hz $CDCl_3$): 148.7, 133.4, 131.6, 127.3, 125.5, 124.9, 122.1, 61.3, 29.85; HRMS (ESI, m/z) calc for $C_{36}H_{32}O_4K$ $(M+K)^+$: 567.1938. Found 567.1939.

Compound **10b**: A solution of **1** [prepared from **2** (238 mg, 0.5 mmol)] and 1,4-triphenylenequinone (258 mg, 2 mmol) in THF (10 mL) was heated at 50 ˚C for 18 h. The precipitate obtained was filtered and was washed with CH_2Cl_2 to afford **10b** as an insoluble white solid (109, 65 %); IR (KBr cm^{-1}); ν 2359, 2332, 1693,1690,1430, 1237, 1095; HRMS (ESI, m/z) calc for $C_{48}H_{33}O_4$. $(M+H)^+$: 673.2379. Found 673.2410.

Compound **10c**: To the suspension of compound **10b** (100 mg, 0.148 mmol) in acetone dimethyl sulphate (112 mg, 0.88 mmol) and potassium carbonate (205 mg, 1.48 mmol) were added under N_2 atmosphere. The reaction mixture was refluxed for 48 h, cooled to room temperature and extracted with chloroform and water. The organic layer was dried over anhydrous sodium sulphate and concentrated using a rotavapour. The crude product was purified by column chromatography to afford compound **10c** as white solid (4.5 mg, 4%); mp 275 ˚C; IR (KBr cm^{-1}); ν 2987, 1580, 1243, 1045; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.40 (d, *J* = 7.6 Hz, 4H), 8.51 (d, *J* = 7.6 Hz, 4H), 7.56 (m, 8H), 6.06 (s, 4H), 3.59 (m,20H); ^{13}C NMR (100 Hz $CDCl_3$): 150.7, 132.3, 130.0, 129.2, 128.3, 127.1, 126.2, 126.1, 125.9, 122.0,59.0, 29.0; HRMS (ESI, m/z) calc for $C_{52}H_{44}O_4Na$ $(M+Na)^+$ 747.3298. Found 747.3298.

Dehydrogenation of 7c to 11 using DDQ:

To a solution of **7c** (42.8mg, 0.1mmol) in 5 mL of toluene was added DDQ (46.5 mg, 0.205mmol) added. The reaction mixture was heated at 100 °C for 2h and allowed to cool to room temperature, extracted with saturated sodium bicarbonate solution and chloroform. The organic layer was dried over anhydrous sodium sulphate, evaporated using a rotavapour and purified by column chromatography to afford **11** as a white solid (40 mg, 94%). IR (KBr, cm^{-1}): ν 2985, 2360, 1468, 1390, 1314, 1195, 1042. ^{1}H NMR (400 MHz, $CDCl_3$): 7.91 (s, 4H), 7.06 (s, 4H), 6.54 (s, 4H), 3.88 (s, 12H), ^{13}C NMR (100 Hz $CDCl_3$): 149.3, 135.1, 133.5, 125.2, 122.0, 103.1, 55.7; HRMS (ESI, m/z) calc for $C_{28}H_{25}O_4$ 425.1753 (M+H), found 425.1738, calc for $C_{28}H_{24}O_4Na$ 447.1572 (M+Na), found 447.1568.

Oxidation of 7b to quinone 12 using MnO_2: To a solution of **7b** (42.8mg, 0.1mmol) in 5mL of toluene was added manganese dioxide (174mg, 20 mmol). The reaction mixture was heated at 100 °C for 2h and allowed to cool to room temperature, filtered

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and washed with chloroform. Solvent was evaporated using a rotavapour to afford **12** as a yellow solid (33.5 mg, 92%); mp ; IR (KBr, cm^{-1}): ν 2961, 1717, 1337, 1284, 1255, 1104; ^1H NMR (400 MHz, $CDCl_3$): 7.78 (s, 4H), 6.95 (s, 4H), 6.91 (s, 4H), ^{13}C NMR (100 Hz $CDCl_3$): 184.4, 142.3, 138.9, 133.8, 130.6, 127.6; HRMS (ESI, m/z) calc for $C_{24}H_{12}O_4K$ 403.0373. Found 403.0383.

Diels-Alder reaction of maleimide with 1: A solution of N-phenylmaleimide (173 mg, 2 mmol) and **1** [prepared from 3 (238 mg, 0.5 mmol)] in toluene (5 mL) was heated at 80 ˚C for 14 h. The solvent was evaporated and residue was purified by chromatography on silica gel (eluant hexane/ethyl acetate, 10:3 v/v) to afford **13b and 13c** (ratio 1.1:1) as a white solid (94 mg, 75%).

Compound **13b**: mp 227 ˚C; IR (KBr, cm^{-1}): ν 2941, 2914, 1776, 1706, 1596, 1502, 1377, 1309, 1173; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (m, 4H), 7.37 (t, *J* = 7.6Hz, 4H) 7.15 (d , *J* = 7.6Hz, 2H), 5.66 (d , *J* = 11.2 Hz, 2H) 5.53 (d, *J* = 11.2 Hz, 2H), 3.21 (s,2H), 3.11 (d, *J* = 2.4 Hz, 2H), 2.50 (m, 4H), 3.33 (m, 2H), 2.17 (m, 2H); ^{13}C NMR (100 Hz $CDCl_3$): ^{13}C NMR (100 Hz $CDCl_3$): 178.7, 178.5, 135.4, 135.3, 133.5, 133.1, 132.2, 132.0, 129.3, 129.1, 128.8, 128.5, 126.5, 125.8, 39.58, 39.52, 29.7, 29.4; HRMS (ESI, m/z) calc for $C_{32}H_{27}N_2O_4$ $(M+H)^+$: 503.1965. Found 503.1979.

Compound **13c**: mp 219 ˚C IR (KBr): ν 2941, 2914, 1776, 1706, 1596, 1502, 1377, 1309, 1173, $cm^{-1;}$ ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, *J* = 7.2 Hz, 4H), 7.37 (t, *J* = 7.6Hz, 2H) 7.17(d , *J* = 8 Hz, 4H), 5.56 (s, 4H) 3.24 (t, *J* = 2Hz, 4H), 2.59(d, *J* = 14.8 Hz, 4H), 2.42 (d, *J* = 13.2 Hz, 4H); ^{13}C NMR (100 Hz $CDCl_3$): 178.7, 135.6, 134.3, 132.0, 129.3, 128.8, 126.5, 39.69, 30.0; HRMS (ESI, m/z) calc for $C_{32}H_{27}N_2O_4$ $(M+H)^+$: 503.1965. Found 503.1961.

Compounds **14b** and **14c** were synthesized by the same procedure as above and were separated by column chromatography.

Compound **14b**: mp 175 ˚C IR (KBr, cm^{-1}): ν 2835, 1704, 1511, 1390,1183; ^1H NMR (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8 Hz, 4H), 6.95 (d, *J* = 8.8 Hz, 4H) 5.55 (s, 4H) 3.81 (s, 6H), 3.22 (t, *J*= 2.2 Hz, 4H), 2.58 (d, *J* = 15.2 Hz, 4H), 2.41 (dd, *J*= 3.8Hz, 16.4Hz,4H); ^{13}C NMR (100 Hz $CDCl_3$): 179.0, 159.7, 135.6, 134.3, 127.7, 124.6, 114.6, 55.6, 39.6, 30.0; HRMS (ESI, m/z) calc for $C_{34}H_{31}N_2O_6$ $(M+H)^+$: 563.2177. Found 563.2175

Compound **14c**: mp 195 ˚C; IR (KBr, cm^{-1}): ν 2845, 1707, 1510, 1441, 1390, 1244, 1180, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d , *J* =9.2 Hz, 4H), 7.05 (d , *J* =9.2 Hz, 2H), 6.97(d , *J* =9.2 Hz, 2H), 6.94 (d , *J* =9.2 Hz, 2H), 5.65(d, *J* = 11.2 Hz, 2H), 5.52 (d, *J* = 11.2 Hz, 2H),3.83 (s, 3H), 3.80 (s, 3H), 3.19 (t, *J* = 3 Hz, 2H), 3.10 (t, *J* = 3 Hz, 2H), 2.52 (d, *J* = 15.2 Hz, 2H), 2.46 (d, *J* = 14.8 Hz, 2H), 2.33 (d, *J* = 13.6 Hz, 2H), 2.175 (d, *J* = 12 Hz, 2H),^{13}C NMR (100 Hz $CDCl_3$): 179.0, 178.7, 159.6, 159.3, 135.4, 135.3, 133.5, 133.1, 127.7, 127.0, 124.8, 124.6, 114.6, 114.3, 55.67, 55.63, 39.5, 39.4, 29.8, 29.4; HRMS (ESI, m/z) calc for $C_{34}H_{31}N_2O_6$. $(M+H)^+$: 563.2177. Found 563.2178.

Conflicts of interest

There are no conflicts to declare

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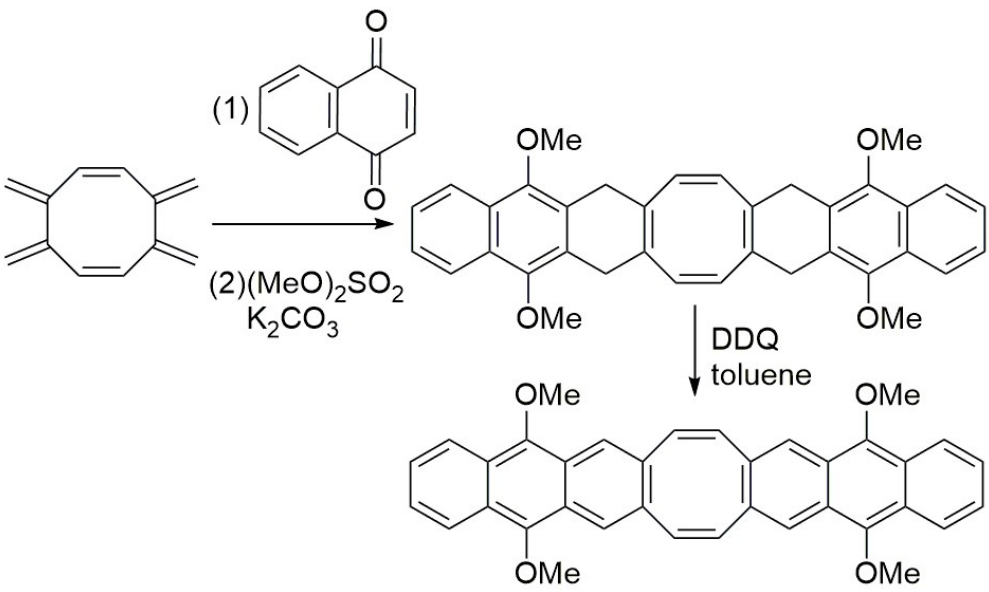

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