One-pot synthesis of cyclophane-type macrocycles using manganese(III)-mediated oxidative radical cyclization

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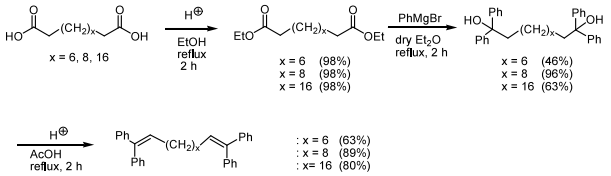
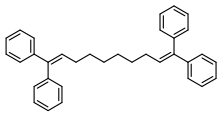
Supplementary data

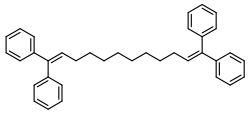
The synthetic procedures and spectroscopic data of the substrates **1$_{(m)}$**, **1$_{(O)}$**, **2$_{(n)}$-arom**, **2$_{(CH2)y}$-arom**, **4$_{(m)}$**, **6**, and **8** with references, and the X-ray data collection and processing parameters of [22]paracyclophane **3$_{(8)(1)}$-*para***.

The terminal alkadienes **1$_{(m)}$** were synthesized by the reaction of the corresponding 1,ω-alkanedicarboxylates with phenylmagnesium bromide followed by acid-catalyzed dehydration.[1,2]

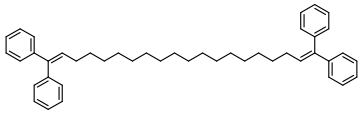




1,1,10,10-Tetraphenyl-1,9-decadiene (1$_{(6)}$): R_f = 0.83 ($CHCl_3$). Colorless microcrystals (from ethanol), m.p. 108-110 °C; IR ($CHCl_3$): ν 1597 (C=C) cm^{-1}. ^{1}H NMR (300MHz, $CDCl_3$): ™ 7.46-7.07 (20H, m, arom. H), 6.05 (2H, t, J = 7.5 Hz, =C*H*-), 2.07 (4H, dt, J = 7.5, 7.5 Hz, -CH_2-), 1.46-1.31 (4H, m, -CH_2-), 1.31-1.17 (4H, m, -CH_2-) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 142.8 (2C, >C=), 141.4, 140.3 (4C, arom. C), 130.2, 129.9, 128.1, 128.0, 127.2 (20C, arom. *C*H), 126.8, 126.7 (2C, =CH-), 29.8, 29.7, 29.0 (6C, -*C*H$_2$-) ppm. Anal. calcd for $C_{34}H_{34}$: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.86.

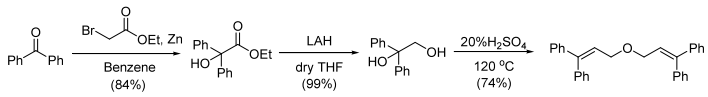


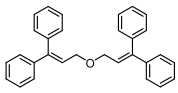
1,1,12,12-Tetraphenyl-1,11-dodecanediene ($\mathbf{1_{(8)}}$): R_f = 0.90 ($CHCl_3$). Colorless microcrystals (from ethanol), m.p. 85-86 °C; IR ($CHCl_3$): ν 1597 (C=C) cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): ™ 7.15-7.38 (20H, m, arom. H), 6.07 (2H, t, J = 7.5 Hz, =C*H*-), 2.10 (4H, q, J = 7.5 Hz, -CH_2-), 1.41 (8H, m, -CH_2-), 1.24 (4H, m, -CH_2-) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 142.8 (2C, >C=), 141.4, 140.3 (4C, arom.C), 130.3, 129.9, 128.1, 127.2 (20C, arom.CH), 126.8, 126.7 (2C, =*C*H-), 29.9, 29.7, 29.4, 29.2 (8C, -*C*H_2-) ppm. FAB HRMS (acetone/NBA): calcd for $C_{36}H_{38}$ 470.2974 (M^+); found 470.2980.



1,1,20,20-Tetraphenyl-1,19-icosanediene ($\mathbf{1_{(16)}}$): R_f = 0.91 ($CHCl_3$). Colorless microcrystals (from ethanol), m.p. 64 °C. IR ($CHCl_3$): ν 1597 (C=C) cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): ™ 7.40-7.14 (20H, m, arom. H), 6.07 (2H, t, J = 7.5 Hz, =C*H*-), 2.10 (4H, q, J = 7.5 Hz, -CH_2-), 1.42 (4H, m, -CH_2-), 1.23 (24H, m, -CH_2-) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 142.7 (2C, >C=), 141.4, 140.3 (4C, arom.C), 130.3, 129.9, 129.4, 128.7, 128.3, 128.05, 128.00, 127.2, 127.1 (20C, arom.CH), 126.75, 126.67 (2C, =*C*H-), 29.9, 29.7, 29.6, 29.5, 29.3 (16C, -*C*H_2-) ppm. FAB HRMS (acetone/NBA): calcd for $C_{44}H_{54}$ 582.4226 (M^+); found 582.4202.

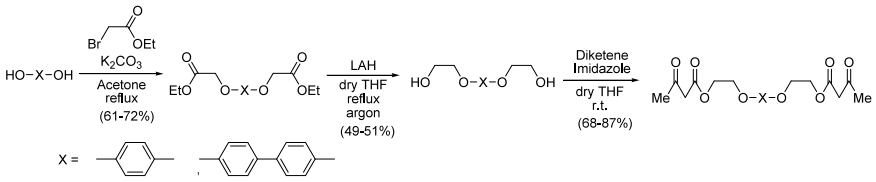
4-Oxa-1,1,7,7-tetraphenylheptadiene ($\mathbf{1_{(O)}}$) was prepared as follows. Alkylation of acetophenone with ethyl bromoacetate and subsequent reduction with lithium aluminum hydride (LAH) gave 1,1-diphenylethane-1,2-diol, which was condensed in 20%H_2SO_4 aqueous solution to give 4-oxa-1,1,7,7-tetraphenylheptadiene ($\mathbf{1_{(O)}}$).[1b]



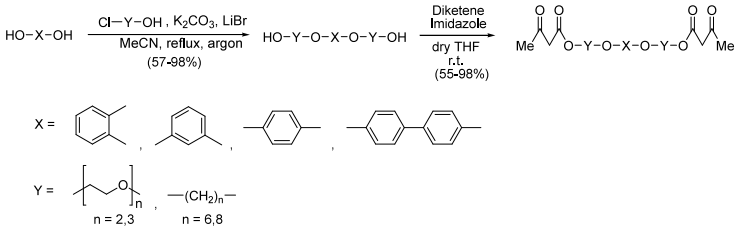


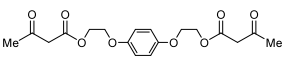
4-Oxa-1,1,7,7-tetraphenylheptadiene ($\mathbf{1_{(O)}}$): R_f = 0.35 ($CHCl_3$:Hexane = 1:5 v/v). Colorless oil. IR ($CHCl_3$): ≀ 1599 (C=C) cm^{-1}. ^1H NMR (300MHz, $CDCl_3$): ™ 7.30-7.09 (20H, m, arom. H), 6.20 (2H, t, J = 6.6 Hz, =C*H*-), 4.01 (4H, d, J = 6.6 Hz,-CH_2-) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 144.6 (2C, >C=), 141.8 (2C, arom. C), 139.1 (2C, arom. C), 129.7, 128.1, 128.0, 127.6, 127.4, 127.4 (20C, arom. *C*H), 125.5 (2C, =CH-), 68.0 (2C, -*C*H_2-) ppm. FAB HRMS (acetone/NBA/NaI): calcd for $C_{30}H_{26}ONa$ 425.1881 (M^++Na); found 425.1895.

Preparation of the bis(3-oxobutanoate)s **2$_{(1)}$-*para*** and **2$_{(1)}$-*biphen*** was as follows. The corresponding phenols were alkylated with ethyl bromoacetate to give the corresponding diesters, which were reduced with LAH to afford the corresponding diols.[3] The diols were converted by the condensation of diketene into bis(3-oxobutanoate)s **2$_{(1)}$-*para*** and **2$_{(1)}$-*biphen***.[1,3]

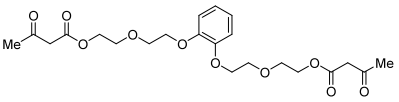


Other bis(3-oxobutanoate)s **2$_{(n)}$-arom** were obtained by the reaction of the corresponding phenols with 2-(2-chloroethoxy)ethanol, 2-[2-(2-chloroethoxy)ethoxy]ethanol, 6-chloro-1-hexanol, or 8-chloro-1-octanol in the presence of potassium carbonate with a catalytic amount of lithium bromide,[5] followed by the condensation of diketene.[1,4]

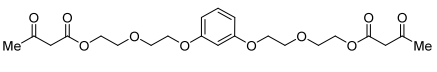




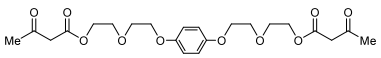
***p*-Phenylenebis(1-oxapropyl) di(3-oxobutanoate) (2$_{(1)}$-*para*)**[6]: R_f = 0.24 ($CHCl_3$). Colorless microcrystals (from $CHCl_3$-hexane), m.p. 84-85 °C. IR ($CHCl_3$): ν 1745, 1717 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.84 (4H, m, arom. H), 4.49-4.46 (4H, m, -C*H*$_2$O-), 4.17-4.13 (4H, m, -C*H*$_2$O-), 3.52, 3.51 (4H, s, -COC*H*$_2$CO-), 2.28, 2.27 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.3 (2C, *C*=O), 167.0 (2C, -*C*O$_2$-), 152.9 (2C, arom. C), 115.7 (4C, arom. *C*H), 66.3 (2C, -*C*H$_2$O-), 63.6 (2C, -*C*H$_2$O-), 49.8 (2C, -CO*C*H$_2$CO-), 30.1 (2C, -*C*H$_3$) ppm.



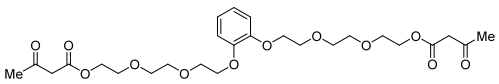
***o*-Phenylenebis(1,4-dioxahexyl) di(3-oxobutanoate) (2$_{(2)}$-*ortho*)**: R_f = 0.30 ($CHCl_3$:MeOH = 98:2 v/v). Colorless liquid. IR ($CHCl_3$): ν 1744, 1717 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): ™ 6.92 (4H, m, arom. H), 4.32 (4H, t, J = 4.8 Hz, -C*H*$_2$O-), 4.16 (4H, t, J = 4.8 Hz, -C*H*$_2$O-), 3.86 (4H, t, J = 4.8 Hz, -C*H*$_2$O-), 3.81 (4H, t, J = 4.8 Hz, -C*H*$_2$O-), 3.48 (4H, s, -COC*H*$_2$CO-), 2.23 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.5 (2C, *C*=O), 167.1 (2C, -*C*O$_2$-), 148.9 (2C, arom. C), 121.7 (2C, arom. *C*H), 114.8 (2C, arom. *C*H), 69.7 (2C, -*C*H$_2$O-), 69.1 (2C, -*C*H$_2$O-), 68.9 (2C, -*C*H$_2$O-), 64.4 (2C, -*C*H$_2$O-), 49.9 (2C, -CO*C*H$_2$CO-), 30.1 (2C, -*C*H$_3$) ppm. FAB HRMS (acetone/NBA/NaI): calcd for $C_{22}H_{30}O_{10}Na$ 477.1737 (M^++Na); found 477.1759.



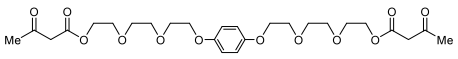
***m*-Phenylenebis(1,4-dioxahexyl) di(3-oxobutanoate) ($2_{(2)}$-*meta*)**: R_f = 0.28 ($CHCl_3$:MeOH = 98:2 v/v). Colorless liquid. IR ($CHCl_3$): ν 1744, 1717 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 7.15 (1H, t, *J* = 8.1 Hz, arom. H), 6.53 (3H, m, arom. H), 4.31 (4H, t, *J* = 4.5 Hz, -C*H*$_2$O-), 4.09 (4H, t, *J* = 4.5 Hz, -C*H*$_2$O-), 3.84-3.81 (4H, m, -C*H*$_2$O-), 3.78-3.75 (4H, m, -C*H*$_2$O-), 3.47 (4H, s, -COC*H*$_2$CO-), 2.23 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.2 (2C, *C*=O), 166.8 (2C, -*C*O_2-), 159.5 (2C, arom. C), 129.5 (1C, arom. *C*H), 106.7 (2C, arom. *C*H), 101.4 (1C, arom. *C*H), 69.2 (2C, -*C*H_2O-), 68.6 (2C, -*C*H_2O-), 67.0 (2C, -*C*H_2O-), 63.9 (2C, -*C*H_2O-), 49.5 (2C, -CO*C*H_2CO-), 29.7 (2C, -*C*H_3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{22}H_{30}O_{10}$ 454.1839 (M^+); found 454.1833.



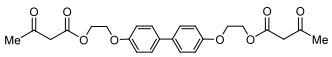
***p*-Phenylenebis(1,4-dioxahexyl) di(3-oxobutanoate) ($2_{(2)}$-*para*)**[7]: R_f = 0.24 ($CHCl_3$). Colorless liquid. IR ($CHCl_3$): ν 1744, 1717 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 6.84 (4H, m, arom. H), 4.33 (4H, t, *J* = 4.8 Hz, -C*H*$_2$O-), 4.07 (4H, t, *J* = 4.8 Hz, -C*H*$_2$O-), 3.84-3.77 (8H, m, -C*H*$_2$O-), 3.48 (4H, s, -COC*H*$_2$CO-), 2.26 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.4 (2C, *C*=O), 167.0 (2C, -*C*O_2-), 152.8 (2C, arom. C), 115.4 (4C, arom. *C*H), 69.6 (2C, -*C*H_2O-), 68.8 (2C, -*C*H_2O-), 67.8 (2C, -*C*H_2O-), 64.1 (2C, -*C*H_2O-), 49.8 (2C, -CO*C*H_2CO-), 30.0 (2C, -*C*H_3) ppm.



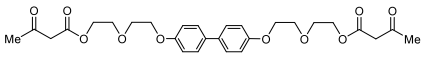
***o*-Phenylenebis(1,4,7-trioxanonanyl) di(3-oxobutanoate) ($2_{(3)}$-*ortho*)**: R_f = 0.24 ($CHCl_3$:MeOH = 98:2 v/v). Colorless liquid. IR ($CHCl_3$): ν 1744, 1717 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 6.92 (4H, m, arom. H), 4.30 (4H, t, *J* = 4.8 Hz, -C*H*$_2$O-), 4.17 (4H, t, *J* = 4.8 Hz, -C*H*$_2$O-), 3.86 (4H, t, *J* = 4.8 Hz, -C*H*$_2$O-), 3.75-3.71 (8H, m, -C*H*$_2$O-), 3.68-3.66 (4H, m, -C*H*$_2$O-), 3.49 (4H, s, -COC*H*$_2$CO-), 2.26 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.6 (2C, *C*=O), 167.1 (2C, -*C*O_2-), 148.9 (2C, arom. C), 121.7 (2C, arom. *C*H), 114.8 (2C, arom. *C*H), 70.8 (2C, -*C*H_2O-), 70.6 (2C, -*C*H_2O-), 69.8 (2C, -*C*H_2O-), 68.9 (2C, -*C*H_2O-), 68.8 (2C, -*C*H_2O-), 64.3 (2C, -*C*H_2O-), 50.0 (2C, -CO*C*H_2CO-), 30.1 (2C, -*C*H_3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{38}O_{12}$ 542.2363 (M^+); found 542.2355.



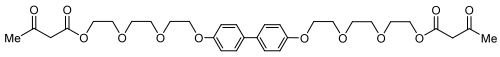
***p*-Phenylenebis(1,4,7-trioxanonanyl) di(3-oxobutanoate) ($2_{(3)}$-*para*)**: R_f = 0.21 ($CHCl_3$:MeOH = 98:2 v/v). Colorless microcrystals (from $CHCl_3$-hexane), m.p. 59-60 °C. IR ($CHCl_3$): ν 1744, 1717 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 6.84 (4H, m, arom. H), 4.31 (4H, t, *J* = 4.8 Hz, -C*H*$_2$O-), 4.07 (4H, t, *J* = 4.8 Hz, -C*H*$_2$O-), 3.83 (4H, t, *J* = 4.8 Hz, -C*H*$_2$O-), 3.74-3.66 (12H, m, -C*H*$_2$O-), 3.48 (4H, s, -COC*H*$_2$CO-), 2.26 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.5 (2C, *C*=O), 167.1 (2C, -*C*O_2-), 153.0 (2C, arom. C), 115.5 (4C, arom. *C*H), 70.7 (2C, -*C*H_2O-), 70.6 (2C, -*C*H_2O-), 69.9 (2C, -*C*H_2O-), 68.9 (2C, -*C*H_2O-), 68.0 (2C, -*C*H_2O-), 64.3 (2C, -*C*H_2O-), 49.9 (2C, -CO*C*H_2CO-), 30.1 (2C, -*C*H_3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{38}O_{12}$ 542.2363 (M^+); found 542.2349.



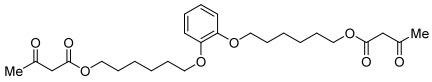
4,4'-Biphenylenebis(1-oxapropyl) di(3-oxobutanoate) ($2_{(1)}$-*biphen*): R_f = 0.51 ($CHCl_3$:MeOH = 95:5 v/v). Colorless microcrystals (from $CHCl_3$-hexane), m.p. 99-100 °C. IR ($CHCl_3$): ν 1746, 1717 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 7.46 (4H, m, arom. H), 6.95 (4H, m, arom. H), 4.54-4.50 (4H, m, -C*H*$_2$O-), 4.24-4.20 (4H, m, -C*H*$_2$O-), 3.514, 3.506 (4H, s, -COC*H*$_2$CO-), 2.28, 2.27 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.3 (2C, *C*=O), 167.1 (2C, -*C*O$_2$-), 157.6 (2C, arom. C), 133.9 (2C, arom. C), 127.8 (4C, arom. *C*H), 114.9 (4C, arom. *C*H), 65.8 (2C, -*C*H$_2$O-), 63.6 (2C, -*C*H$_2$O-), 49.9 (2C, -CO*C*H$_2$CO-), 30.2 (2C, -*C*H$_3$) ppm. Anal Calcd for $C_{24}H_{26}O_8$•1/3H_2O: C, 64.28; H, 5.99. Found: C, 64.38; H, 5.89.



4,4'-Biphenylenebis(1,4-dioxahexyl) di(3-oxobutanoate) ($2_{(2)}$-*biphen*): R_f = 0.15 ($CHCl_3$). Colorless microcrystals (from $CHCl_3$-hexane), m.p. 84-85 °C. IR ($CHCl_3$): ν 1744, 1717 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 7.46 (4H, m, arom. H), 6.95 (4H, m, arom. H), 4.34 (4H, td, *J* = 4.8, 1.5 Hz, -C*H*$_2$O-), 4.15 (4H, td, *J* = 4.8, 1.5 Hz, -C*H*$_2$O-), 3.88 (4H, td, *J* = 4.5, 1.5 Hz, -C*H*$_2$O-), 3.81 (4H, td, *J* = 4.5, 1.5 Hz, -C*H*$_2$O-), 3.48 (4H, s, -COC*H*$_2$CO-), 2.27 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.5 (2C, *C*=O), 167.1 (2C, -*C*O$_2$-), 157.8 (2C, arom. C), 133.6 (2C, arom. C), 127.7 (4C, arom. *C*H), 114.9 (4C, arom. *C*H), 69.7 (2C, -*C*H$_2$O-), 69.1 (2C, -*C*H$_2$O-), 67.5 (2C, -*C*H$_2$O-), 64.3 (2C, -*C*H$_2$O-), 50.0 (2C, -CO*C*H$_2$CO-), 30.2 (2C, -*C*H$_3$) ppm. Anal Calcd for $C_{28}H_{34}O_{10}$·1/5H_2O: C, 62.96; H, 6.49. Found: C, 63.12; H, 6.43.

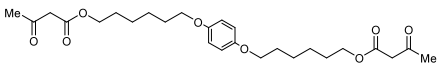


4,4'-Biphenylenebis(1,4,7-trioxanonanyl) di(3-oxobutanoate) ($2_{(3)}$-*biphen*): R_f = 0.12 ($CHCl_3$:MeOH = 98:2 v/v). Colorless microcrystals (from $CHCl_3$-hexane), m.p. 84-85 °C. IR ($CHCl_3$): ν 1744, 1717 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 7.46 (4H, m, arom. H), 6.96 (4H, m, arom. H), 4.31 (4H, t, *J* = 4.5, -C*H*$_2$O-), 4.16 (4H, t, *J* = 4.5 Hz, -C*H*$_2$O-), 3.87 (4H, t, *J* = 4.5 Hz, -C*H*$_2$O-), 3.74-3.67 (12H, m, -C*H*$_2$O-), 3.48 (4H, s, -COC*H*$_2$CO-), 2.26 (6H, s, -C*H*$_3$) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.5 (2C, *C*=O), 167.1 (2C, -*C*O$_2$-), 157.9 (2C, arom. C), 133.5 (2C, arom. C), 127.7 (4C, arom. *C*H), 114.9 (4C, arom. *C*H), 70.8 (2C, -*C*H$_2$O-), 70.6 (2C, -*C*H$_2$O-), 69.8 (2C, -*C*H$_2$O-), 68.9 (2C, -*C*H$_2$O-), 67.5 (2C, -*C*H$_2$O-), 64.3 (2C, -*C*H$_2$O-), 50.0 (2C, -CO*C*H$_2$CO-), 30.1 (2C, -*C*H$_3$). Anal Calcd for $C_{32}H_{42}O_{12}$•1/5H_2O: C, 61.76; H, 6.87. Found: C, 61.86; H, 6.89.

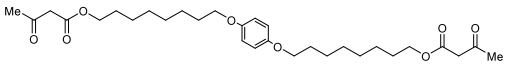


***o*-Phenylenebis(1-oxaheptyl) di(3-oxobutanoate) ($2_{(CH2)6}$-*ortho*)**: R_f = 0.30 ($CHCl_3$:MeOH = 98:2 v/v). Colorless oil. IR ($CHCl_3$): ν 1717 1734 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 6.89 (4H,

m, arom. H), 4.15 (4H, t, J = 6.6 Hz, -CH_2O-), 4.00 (4H, t, J = 6.6 Hz, -CH_2O-), 3.45 (4H, s, -COCH_2CO-), 2.27 (6H, s, -CH_3), 1.85-1.80, 1.71-1.66, 1.52-1.43 (16H, m, -CH_2-) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.6 (2C, *C*=O), 167.2 (2C, -*C*O_2-), 149.0 (2C, arom. C), 121.1 (2C, arom. *C*H), 114.0 (2C, arom. *C*H), 68.9 (2C, -*C*H_2O-), 65.3 (2C, -*C*H_2O-), 50.0 (2C, -CO*C*H_2CO-), 30.1 (2C, -*C*H_3), 29.1, 28.4, 25.64, 25.57 (8C, -CH_2-) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{38}O_8$ 478.2567 (M^+); found 478.2545.

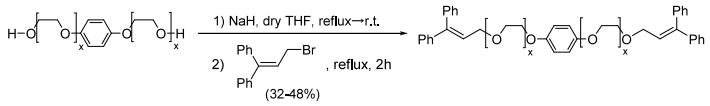


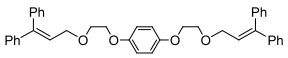
***p*-Phenylenebis(1-oxaheptyl) di(3-oxobutanoate) ($2_{(CH2)6}$-*para*)**: R_f = 0.36 ($CHCl_3$:MeOH = 98:2 v/v). Colorless microcrystals (from $CHCl_3$-hexane), m.p. 42-43 °C. IR ($CHCl_3$): ν 1717, 1734 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): ™ 6.81 (4H, m, arom. H), 4.15 (4H, t, J = 6.6 Hz, -CH_2O-), 3.90 (4H, t, J = 6.6 Hz, -CH_2O-), 3.45 (4H, s, -COCH_2CO-), 2.27 (6H, s, -CH_3), 1.79-1.66, 1.52-1.42 (16H, m, -CH_2-) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.7 (2C, *C*=O), 167.2 (2C, -*C*O_2-), 153.1 (2C, arom. C), 115.3 (4C, arom. *C*H), 68.3 (2C, -*C*H_2O-), 65.4 (2C, -*C*H_2O-), 50.1 (2C, -CO*C*H_2CO-), 30.1 (2C, -*C*H_3), 29.2, 28.4, 25.7, 25.6 (8C, -CH_2-) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{38}O_8$ 478.2567 (M^+); found 478.2567.



***p*-Phenylenebis(1-oxanonyl) di(3-oxobutanoate) ($2_{(CH2)8}$-*para*)**: R_f = 0.35 ($CHCl_3$:MeOH = 98:2 v/v). Colorless microcrystals (from $CHCl_3$-hexane), m.p. 58-59 °C. IR ($CHCl_3$): ν 1717, 1740 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) ™ 6.81 (4H, m, arom. H), 4.14 (4H, t, J = 6.6 Hz, -CH_2O-), 3.89 (4H, t, J = 6.6 Hz, -CH_2O-), 3.45 (4H, s, -COCH_2CO-), 2.27 (6H, s, -CH_3), 1.77-1.63, 1.44-1.35 (24H, m, -CH_2-) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.5 (2C, *C*=O), 167.0 (2C, -*C*O_2-), 153.0 (2C, arom. C), 115.2 (4C, arom. *C*H), 68.4 (2C, -*C*H_2O-), 65.3 (2C, -*C*H_2O-), 49.9 (2C, -CO*C*H_2CO-), 30.0 (2C, -*C*H_3), 29.2, 29.1, 28.9, 28.3, 25.8, 25.6 (12C, -CH_2-) ppm. FAB HRMS (acetone/NBA): calcd for $C_{30}H_{46}O_8$ 534.3193 (M^+); found 534.3204.

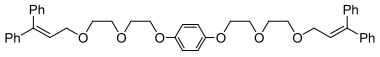
The oxamethylene-tethered terminal dienes $\mathbf{4_{(m)}}$ were prepared by the Williamson ether synthesis of the corresponding diols with 1,1-diphenyl-3-bromopropene which was synthesized by the bromination of 1,1-diphenylpropene.[8,9]



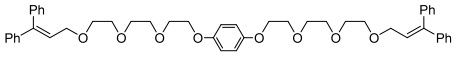


***p*-Phenylenebis(1,4-dioxa-7,7-diphenyl-6-heptene) ($\mathbf{4_{(1)}}$)**: R_f = 0.50 ($CHCl_3$). Yellow oil. IR

($CHCl_3$): ν 1599 (C=C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 7.39-7.17 (20H, m, arom. H), 6.82 (4H, m, arom. H), 6.26 (2H, t, J = 6.6 Hz, =C*H*-), 4.15 (4H, d, J = 6.6 Hz, =CHCH_2-), 4.05 (4H, t, J = 4.8 Hz, -OCH_2-), 3.74 (4H, J = 4.8 Hz, -OCH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): ™ 153.0 (2C, >C=), 144.9 (2C, arom. C), 141.8 (2C, arom. C), 139.2 (2C, arom. C), 129.8, 128.2, 128.1, 127.6, 127.54, 127.50 (20C, arom. CH), 125.4 (2C, =*C*H-), 115.5 (4C, arom. *C*H), 69.0, 68.7, 67.9 (6C, -OCH_2-) ppm. FAB HRMS (acetone/NBA): calcd for $C_{40}H_{38}O_4$ 582.2770 (M^+); found 582.2787.

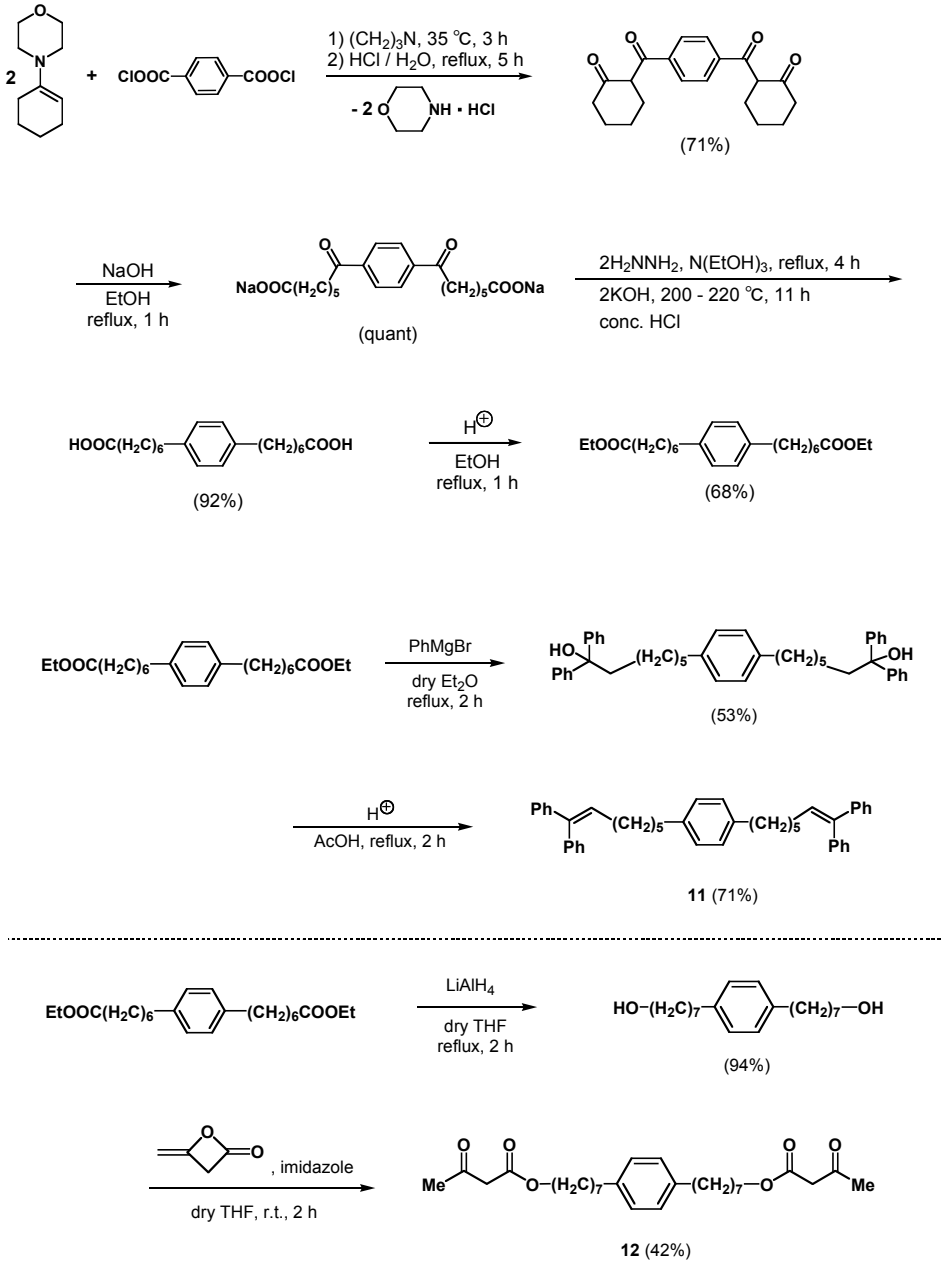


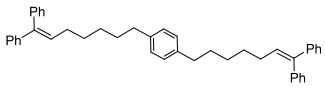
***p*-Phenylenebis(1,4,7-trioxa-10,10-diphenyl-9-decene) ($4_{(2)}$)**: R_f = 0.17 ($CHCl_3$). Yellow oil. IR ($CHCl_3$): ν 1599 (C=C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 7.34-7.14 (20H, m, arom. H), 6.82 (4H, m, arom. H), 6.25 (2H, t, J = 6.6 Hz, =C*H*-), 4.10 (4H, d, J = 6.6 Hz, =CHCH_2-), 4.05 (4H, t, J = 4.8 Hz, -OCH_2-), 3.80 (4H, J = 4.8 Hz, -OCH_2-), 3.71-3.67 (4H, m, -OCH_2-), 3.60-3.57 (4H, m, -OCH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): ™ 152.9 (2C, >C=), 144.4 (2C, arom. C), 141.7 (2C, arom. C), 139.1 (2C, arom. C), 129.6, 128.03, 128.00, 127.5, 127.4 (20C, arom. CH), 125.4 (2C, =*C*H-), 115.4 (4C, arom. *C*H), 70.7, 69.7, 69.4, 68.8, 67.9 (10C, -OCH_2-) ppm. FAB HRMS (acetone/NBA/NaI): calcd for $C_{44}H_{46}O_6Na$ 693.3192 (M^+ +Na); found 693.3229.



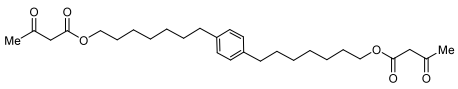
***p*-Phenylenebis(1,4,7,10-tetraoxa-13,13-diphenyl-12-tridecene) ($4_{(3)}$)**: R_f = 0.18 ($CHCl_3$). Yellow oil. IR ($CHCl_3$): ν 1599 (C=C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 7.38-7.14 (20H, m, arom. H), 6.82 (4H, m, arom. H), 6.23 (2H, t, J = 6.6 Hz, =C*H*-), 4.09 (4H, d, J = 6.6 Hz, =CHCH_2-), 4.05 (4H, t, J = 4.8 Hz, -OCH_2-), 3.81 (4H, J = 4.8 Hz, -OCH_2-), 3.73-3.70 (6H, m, -OCH_2-), 3.68-3.63 (6H, m, -OCH_2-), 3.59-3.55 (4H, m, -OCH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): ™ 153.0 (2C, >C=), 144.5 (2C, arom. C), 141.8 (2C, arom. C), 139.2 (2C, arom. C), 130.1, 129.7, 128.9, 128.5, 128.1, 127.6, 127.5 (20C, arom. CH), 125.6 (2C, =*C*H-), 115.5 (4C, arom. *C*H), 70.7, 70.6, 69.8, 69.5, 68.9, 68.0 (14C, -OCH_2-) ppm. FAB HRMS (acetone/NBA/NaI): calcd for $C_{48}H_{54}O_8Na$ 781.3716 (M^+ +Na); found 781.3727.

p-Phenylenebis(7,7-diphenyl-6-heptene) **6** and *p*-phenylenebis(heptyl) bis(3-oxobutanoate) **8** were prepared as follows. The reaction of terephthaloyl dichloride with 1-morpholino-1-cyclohexene followed by the decomposition with sodium hydroxide in ethanol, the Wolff-Kishner reduction,[10] and then esterification gave diethyl *p*-phenylenebis(heptanoate). The *p*-phenylenebis(heptanoate) underwent the Grignard reaction followed by dehydration to give *p*-Phenylenebis(7,7-diphenyl-6-heptene) **6**. While the reduction of the *p*-phenylenebis(heptanoate) followed by esterification with diketene to give *p*-phenylenebis(heptyl) bis(3-oxobutanoate) **8**.[1,4]





***p*-Phenylenebis(7,7-diphenyl-6-heptene) (6)**: R_f = 0.50 ($CHCl_3$). Colorless microcrystals (from $CHCl_3$-hexane), m.p. 76-77 °C. IR ($CHCl_3$): ν 1599 (C=C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ^{TM} 7.38-7.14 (20H, m, arom. H), 7.04 (4H, m, arom. H), 6.06 (2H, t, J = 6.6 Hz, =C*H*-), 2.53 (4H, t, J = 7.3 Hz, -CH_2-), 2.09 (4H, q, J = 7.2 Hz, =CHCH_2-),1.57-1.37 (8H, m, -CH_2-), 1.35-1.30 (4H, m, -CH_2-) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): ^{TM} 142.8 (2C, >C=), 141.4 (2C, arom. C), 140.2 (2C, arom. C), 139.9 (2C, arom. C), 130.2, 130.0 (4C, arom. C), 128.2, 128.1, 128.0, 127.7, 127.2, 126.8 (20C, arom.CH), 126.7 (2C, =*C*H-), 35.4, 31.4, 29.8, 29.6, 28.9 (10C, -CH_2-) ppm. FAB HRMS (acetone/NBA): calcd for $C_{44}H_{46}$ 574.3600 (M^+); found 574.3601.



***p*-Phenylenebis(heptyl) bis(3-oxobutanoate) (8)**: R_f = 0.27 ($CHCl_3$). Colorless oil. IR ($CHCl_3$): ν 1740, 1717 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): ™ 7.07 (4H, m, arom. H), 4.12 (4H, t, J = 6.6 Hz, -CH_2O-), 3.44 (4H, s, -COCH_2CO-), 2.56 (4H, t, J = 7.2 Hz, -PhCH_2-), 2.20 (6H, s, -CH_3), 1.61-1.35, 1.34-1.20 (20H, m, -CH_2-) ppm. ^{13}C NMR (75MHz, $CDCl_3$): ™ 200.4 (2C, *C*=O), 167.0 (2C, -*C*O_2-), 139.7 (2C, arom. C), 128.1 (4C, arom. *C*H), 65.3 (2C, -*C*H_2O-), 49.9 (2C, -CO*C*H_2CO-), 35.3, 31.3 (4C, -CH_2-), 30.0 (2C, -*C*H_3), 29.0, 28.9, 28.3, 25.6 (8C, -CH_2-) ppm. FAB HRMS (acetone/NBA): calcd for $C_{28}H_{43}O_6$ 475.3060 (M+H); found 475.3062.

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Table 5. The X-ray data collection and processing parameters of [22]paracyclophane **3$_{(8)(1)}$-*para***

A. Crystal Data	
Empirical Formula	$C_{54}H_{56}O_8$
Formula Weight	833.03
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.90 X 0.80 X 0.70 mm
Crystal System	monoclinic
Lattice Type	C-centered
No. of Reflections Used for Unit	
Cell Determination (2q range)	25 (30.1 - 34.2°)
Omega Scan Peak Width at Half-height	0.27°
Lattice Parameters	a = 14.5489(17) Å
	b = 31.423(9) Å
	c = 11.6090(13) Å
	β = 118.413(8)°
	V = 4668.0(14) Å^3
Space Group	C2/c (#15)
Z value	4
Dcalc	1.185 g/cm^3
F000	1776.00
m(Mo $K\alpha$)	0.784 cm^{-1}
B. Intensity Measurements	
Diffractometer	Rigaku AFC7R
Radiation	Mo $K\alpha$ (λ = 0.71069 Å)
	graphite monochromated
Attenuator	Zr foil (factor = 8.43)
Take-off Angle	6.0°
Detector Aperture	3.0 mm horizontal
	3.0 mm vertical
Crystal to Detector Distance	235 mm
Voltage, Current	50 kV, 100 mA
Temperature	25.0 °C
Scan Type	ω
Scan Rate	16.0°/min (in w) (up to 2 scans)
Scan Width	(1.73 + 0.30 *tan* θ)°
2θmax	55.0°
No. of Reflections Measured	Total: 6419
	Unique: 5364 (R_{int} = 0.124)
Corrections	Lorentz-polarization

	Absorption (trans. factors: 0.735 - 0.947) Decay (36.48% decline) Secondary Extinction (coefficient: 2.45440e+002)

C. Structure Solution and Refinement	
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$1/\sigma^2(Fo^2) = 1/\sigma^2(Fo)/(4Fo^2)$
$2\theta_{max}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>2.00\sigma(I)$)	2891
No. Variables	309
Reflection/Parameter Ratio	9.36
Residuals: R^1 ($I>2.00\sigma(I)$)	0.0878
Residuals: wR^2 ($I>2.00\sigma(I)$)	0.1042
Goodness of Fit Indicator	4.749
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.86 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.77 $e^-/Å^3$

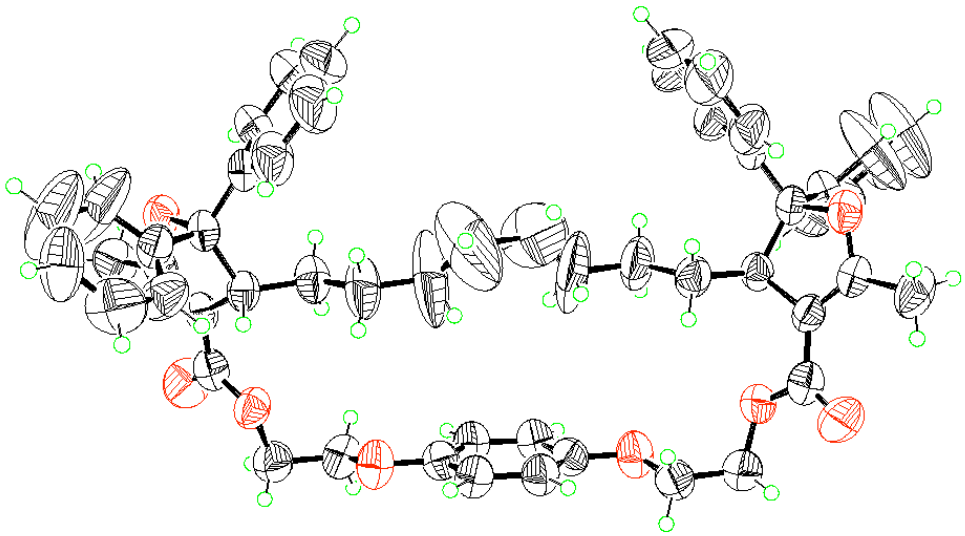

Figure 3. ORTEP Drawing of [22]paracyclophane **3**$_{(8)(1)}$-***para***