Supplementary Materials

Simple one−pot synthesis of hexakis(2-alkoxy-1,5-phenyleneimine) macrocycles by precipitation−driven cyclization

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Experimental procedures

Figure S24. ^{1}H−NMR spectrum of 2-((*S*)-(−)-3,7-dimethyloctyloxy)-5-nitrobenzaldehyde diethyl acetal.

Figure S25. ^{13}C−NMR spectrum of 2-((*S*)-(−)-3,7-dimethyloctyloxy)-5-nitrobenzaldehyde diethyl acetal.

Figure S26. ^{1}H−NMR spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde diethylacetal.

Figure S27. ^{13}C−NMR spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde diethylacetal.

Figure S28. FT−IR spectrum of hexakis(2-octyloxy-1,5-phenyleneimine) macrocycle OcO−Cm6.

Figure S29. ^{1}H−NMR spectrum of hexakis(2-octyloxy-1,5-phenyleneimine) macrocycle (OcO−Cm6) in $CDCl_3$.

Figure S30. FT−IR spectrum of hexakis(2-((*S*)-(−)-3,7-dimethyloctyloxy)-1,5-phenyleneimine) macrocycle ((−)BCO−Cm6).

Figure S31. ^{1}H−NMR spectrum of hexakis(2-((*S*)-(−)-3,7-dimethyloctyloxy)-1,5-phenyleneimine) macrocycle ((−)BCO−Cm6) in $CDCl_3$.

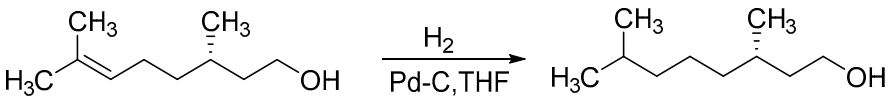
Figure S32. ^{13}C−NMR spectrum of hexakis(2-((*S*)-(−)-3,7-dimethyloctyloxy)-1,5-phenyleneimine) macrocycle ((−)BCO−Cm6) in $CDCl_3$.

Experimental procedures

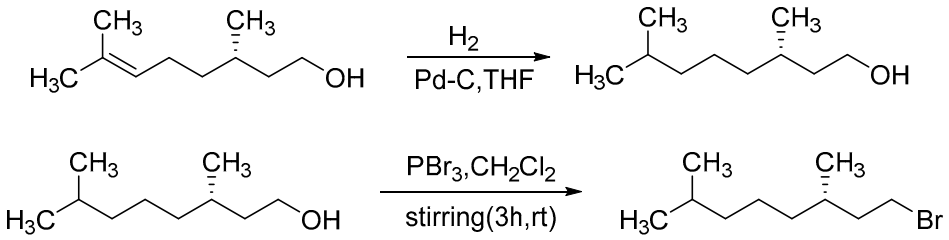
Synthesis of (S)-(−)-1-bromo-3,7-dimethyloctane

(−)-β-citronellol ((*S*)-(−)-3,7-dimethyl-6-octen-1-ol) (20.0 g, 0.128 mol), 5%Pd/C (1.50 g, 0.70 mmol as Pd), and tetrahydrofuran (solvent, 50 ml) were placed in a 100−mL glass-autoclave (TEM−V100, TAIATSU TECHNO Corp., Tokyo, Japan) equipped with a mechanical stirrer and a thermocouple. Hydrogen gas was supplied to the apparatus for 48 h at room temperature while maintaining a constant pressure of 1 MPa. The catalyst was filtered off through Celite® and the filtrate was dried with $MgSO_4$, then condensed to dryness by evaporation to give (*S*)-(−)-3,7-dimethyloctan-1-ol as a colorless liquid (yield 18.91g, 93%). (Scheme S1)

In a 200−mL pear−shaped flask were placed (*S*)-(−)-3,7-dimethyloctan-1-ol (18.9 g, 0.119 mol), dichloromethane (100 ml), and PBr_3 (25 g, 0.092 mol) was added gradually to the solution. The mixture was stirred magnetically at room temperature for 3 h. Water (100 mL) was added dropwise in order to decompose the unreacted PBr_3. The product was extracted with dichloromethane (100 mL) three times and the combined extract was dried over $MgSO_4$. The filtrate was concentrated by evaporation, then was distilled under reduced pressure to give (*S*)-(−)-1-bromo-3,7-dimethyloctane as a colorless liquid (b.p. 58 ^{o}C/3 mmHg). Yield: 9.58 g (36%). (Scheme S2)



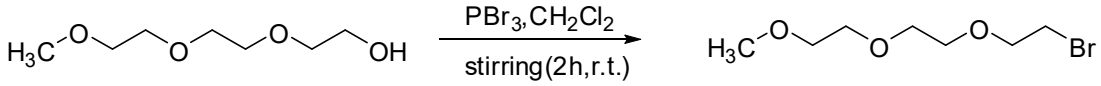
Scheme S1. Synthesis of (*S*)-(−)-3,7-dimethyloctan-1-ol.



Scheme S2. Synthesis of (*S*)-(−)-1-bromo-3,7-dimethyloctane.

Synthesis of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane

Triethylene glycol monomethyl ether (2-(2-(2-methoxyethoxy)ethoxy)ethanol) (30.35 g, 0.185 mol) and dichloromethane (100 ml) were placed in a 200−mL pear−shaped flask. PBr_3 (25 g, 0.092 mol) was then gradually added to the solution. The mixture was magnetically stirred at room temperature for 3 h. Following a similar procedure as mentioned above, 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane was obtained as a colorless liquid (b.p. 78 ºC/4 mmHg). The yield was 19.06 g (45%).



Scheme S3. Synthesis of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane.

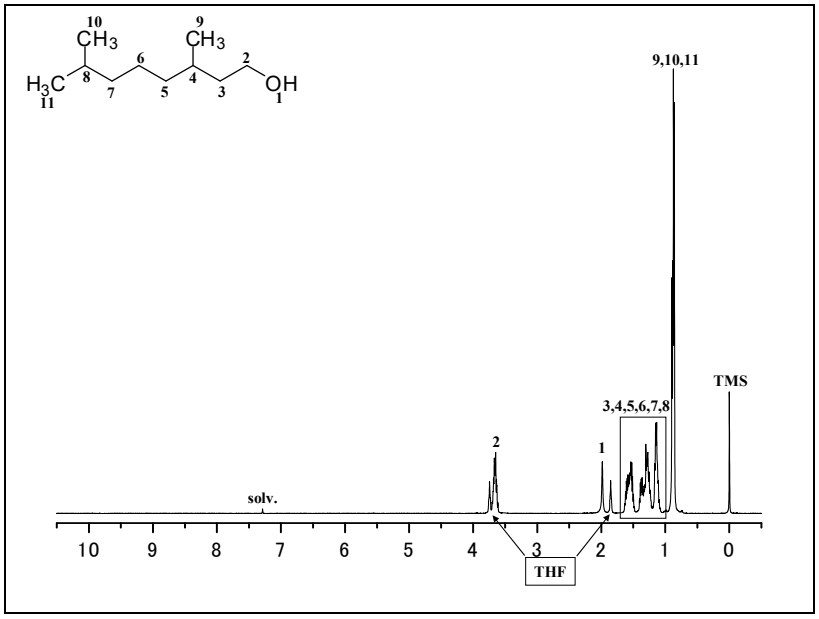


Figure S1. ^{1}H−NMR spectrum of (*S*)-(−)-3,7-dimethyloctan-1-ol; solvent: $CDCl_3$.

^{1}H−NMR (δ, ppm): 0.87(d,J=6.7Hz,6H), 0.89(d,J=6.4Hz,3H), 1.08-1.16(m,3H), 1.20-1.40(m,4H), 1.47-1.63(m,3H),1.98(s,1H), 3.61-3.70(m,2H).

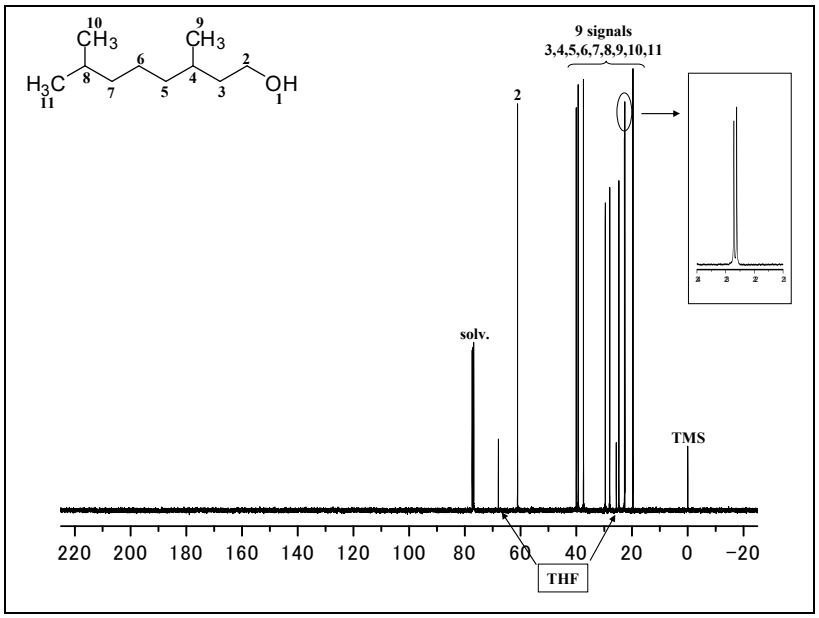


Figure S2. ^{13}C−NMR spectrum of (*S*)-(−)-3,7-dimethyloctan-1-ol; solvent: $CDCl_3$.

^{13}C−NMR (δ, ppm): 19.66, 22.61, 22.71, 24.71, 27.99, 29.57, 37.44, 39.31, 40.02, 61.11.

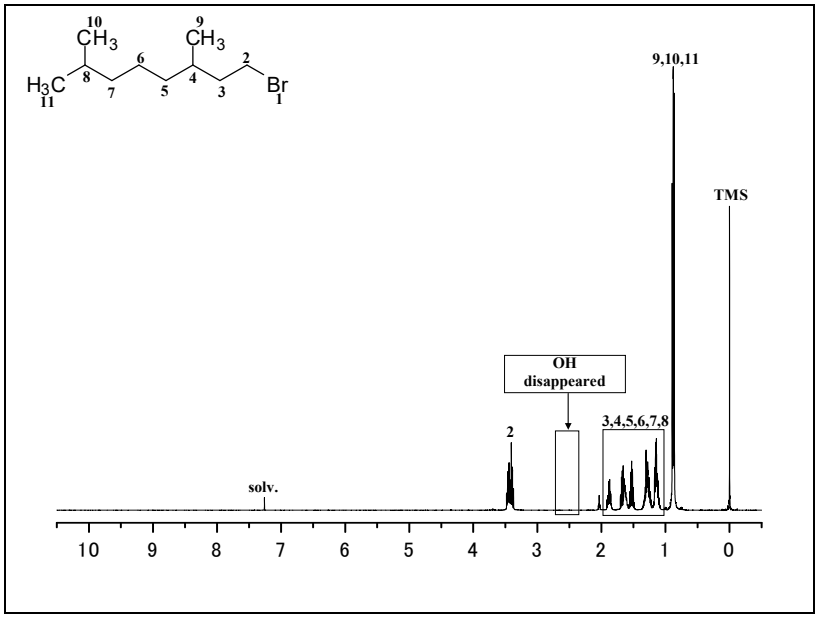


Figure S3. ^{1}H−NMR spectrum of (*S*)-(−)-1-bromo-3,7-dimethyloctane; solvent: $CDCl_3$.

^{1}H−NMR (δ, ppm): 0.87(d,J=6.7Hz,6H), 0.89(d,J=6.4Hz,3H), 1.10-1.16(m,3H), 1.22-1.33(m,3H), 1.48-1.56(m,1H), 1.16-1.70(m,2H), 1.85-1.91(m,1H), 3.37-3.48(m,2H).

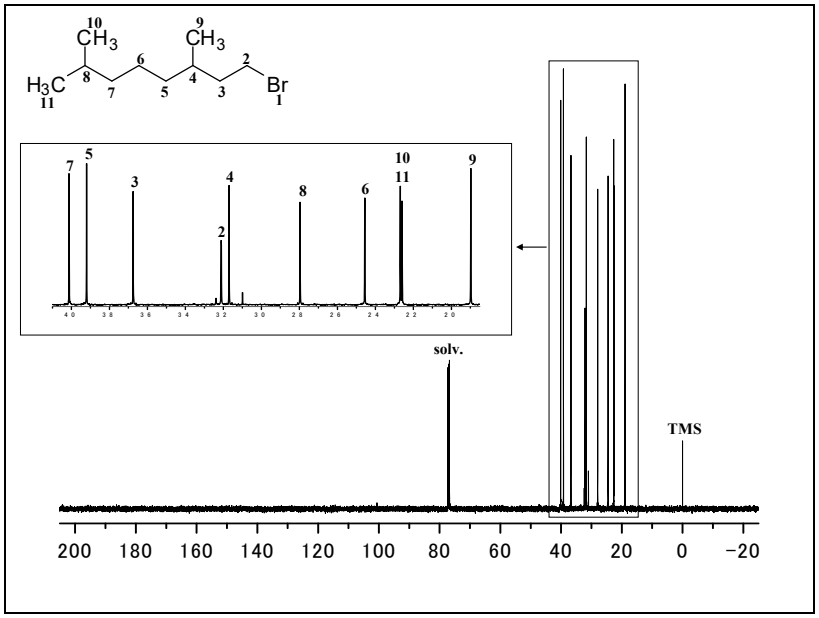


Figure S4. $^{13}C-NMR$ spectrum of (*S*)-(−)-1-bromo-3,7-dimethyloctane; solvent: $CDCl_3$.

$^{13}C-NMR$ (δ, ppm): 18.91, 22.59, 22.68, 24.55, 27.95, 31.70, 32.11, 36.75, 39.20, 40.12.

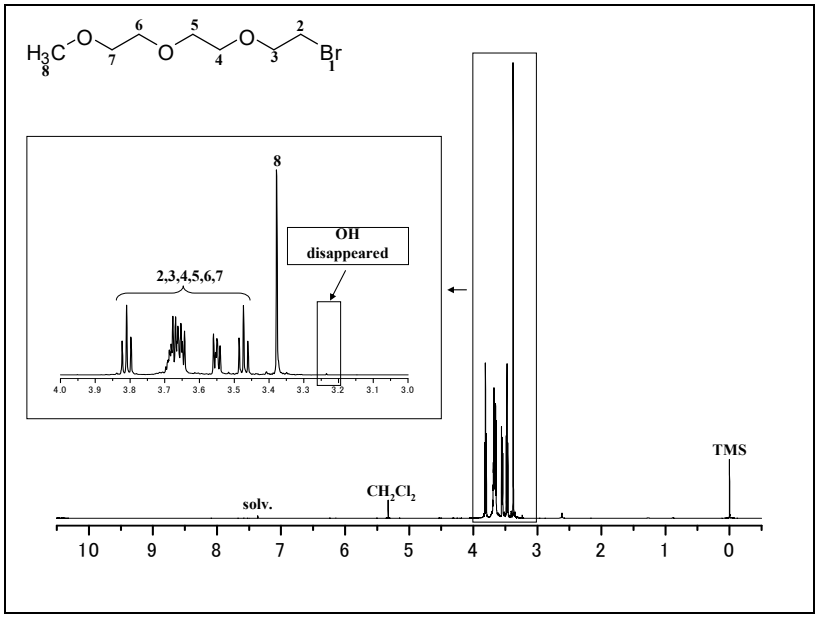


Figure S5. $^{1}H-NMR$ spectrum of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane; solvent: $CDCl_3$.

$^{1}H-NMR$ (δ, ppm): 3.37(s,3H), 3.47(t,J=6.4Hz,2H), 3.54(t,J=4.5Hz,2H), 3.64−3.69(m,6H), 3.80(t,J=6.1Hz,2H).

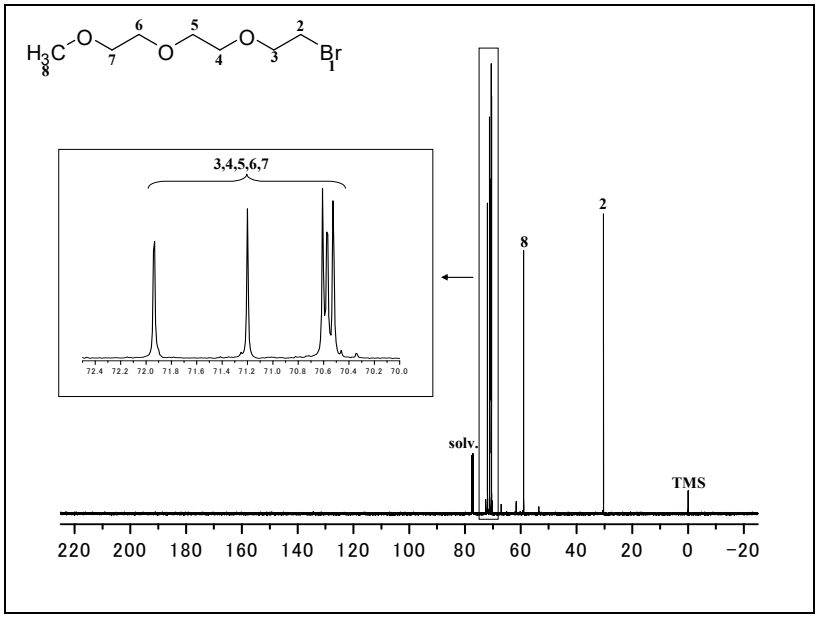


Figure S6. ^{13}C−NMR spectrum of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane; solvent: $CDCl_3$.

^{13}C−NMR (δ, ppm): 30.32, 58.96, 70.52, 70.57, 70.60, 71.20, 71.93.

2-Octyloxy-5-nitrobenzaldehyde

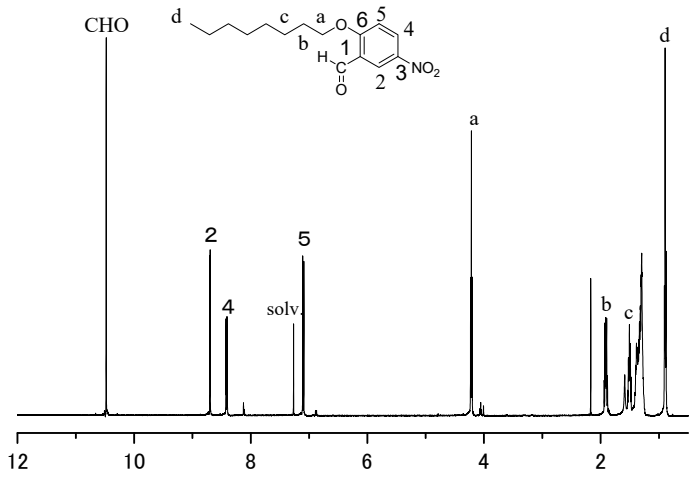


Figure S7. ^{1}H−NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde; solvent: $CDCl_3$.

^{1}H−NMR (δ, ppm): 0.89(t,J=6.1Hz,3H,H−d), 1.30(m,8H), 1.51(quin,J=7.7Hz,2H,H−c), 1.91(quin,J=6.7Hz,2H,H−b), 4.22(t,J=6.4Hz,2H,H−a), 7.10(d,J=9.2,1H,H−5), 8.41(quar,J=6.1Hz,1H,H−4), 8.69(d,J=2.8Hz,1H,H−2), 10.48(s,1H,CHO).

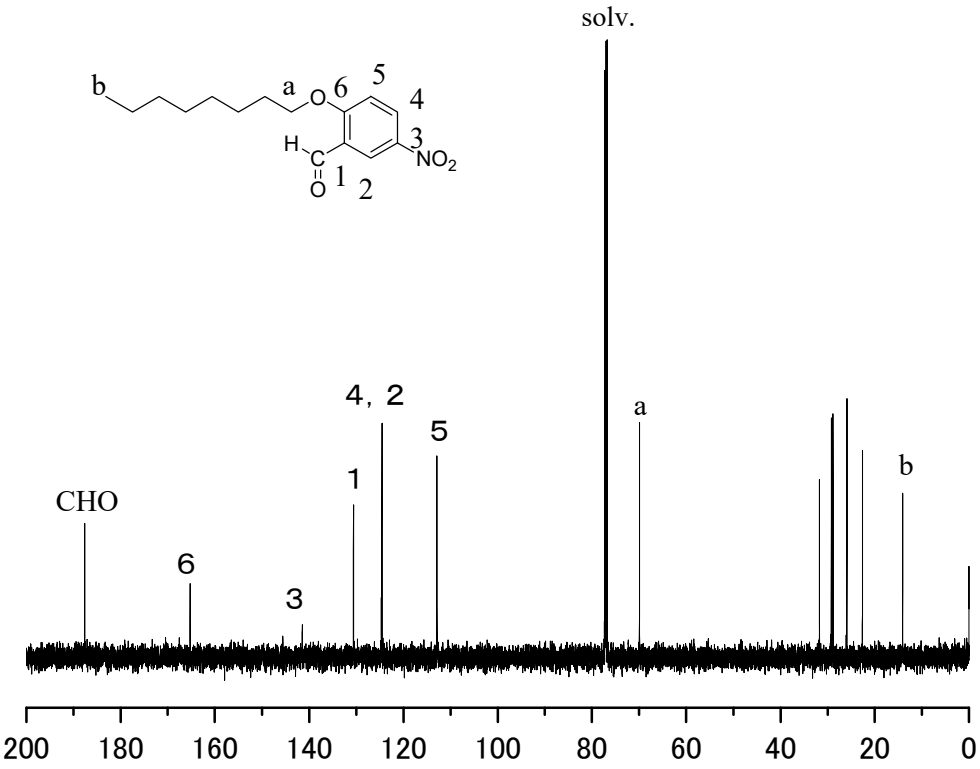


Figure S8. ^{13}C−NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde; solvent: $CDCl_3$.
^{13}C−NMR (δ, ppm): 14.1(C−b), 28.9, 29.16, 29.23, 31.8, 69.9(C−a), 112.9(C−5), 124.5(C−2), 124.7(C−4), 130.6(C−1), 141.5(C−3), 165.3(C−6), 187.6(CHO).

2-((*S*)-(−)-3,7-Dimethyloctyloxy)-5-nitrobenzaldehyde

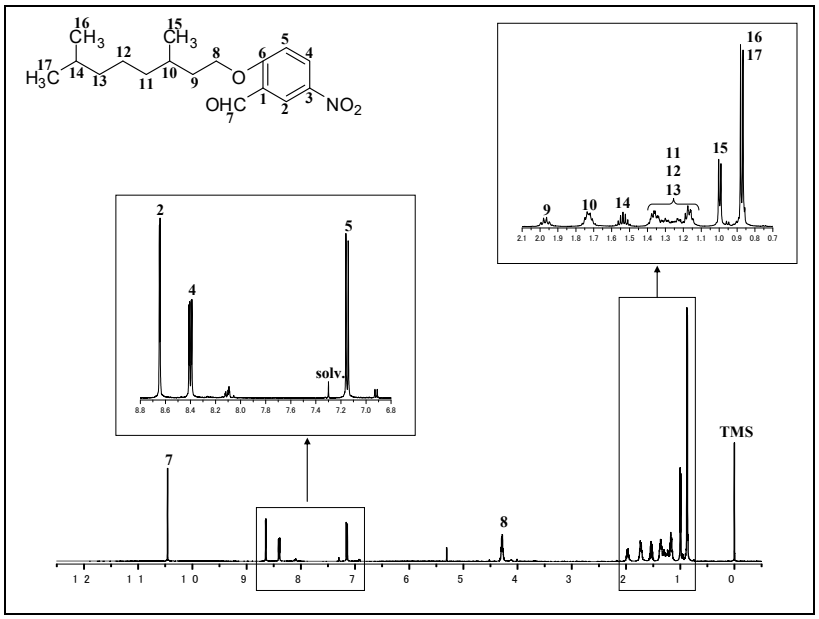


Figure S9. ^{1}H−NMR spectrum of 2-((*S*)-(−)-3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: $CDCl_3$.
^{1}H−NMR (δ, ppm): 0.87(d,J=6.7Hz,6H), 1.00(d,J=6.1Hz,3H), 1.14−1.39(m,6H), 1.49−1.57(m,1H), 1.93−1.99(m,2H), 4.25−4.32(m,2H), 7.15(d,J=9.1Hz,1H), 8.40(d,J=9.4Hz,1H), 8.64(d,J=2.7Hz,1H), 10.45(s,1H).

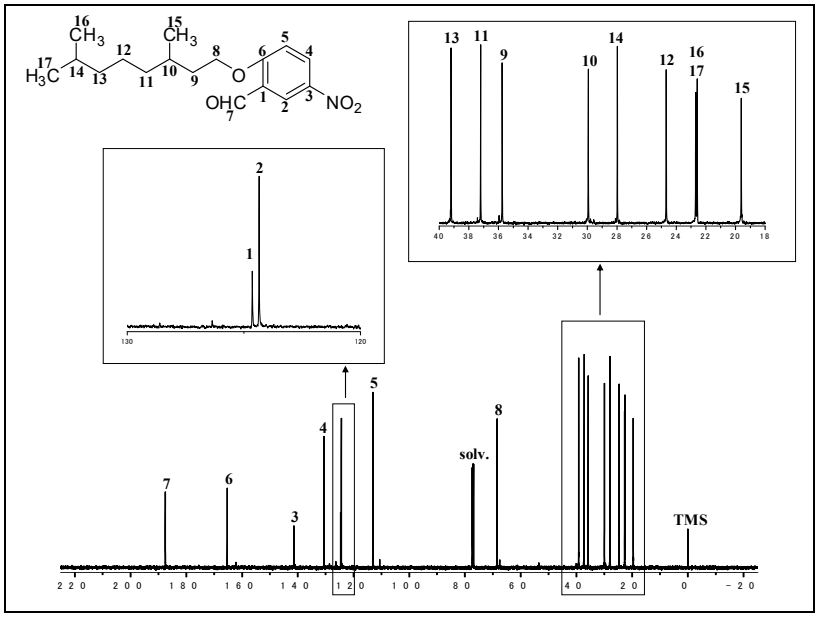


Figure S10. ^{13}C−NMR spectrum of 2-((*S*)-(−)-3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: $CDCl_3$.
^{13}C−NMR (δ, ppm): 19.6, 22.6, 22.7, 24.7, 28.0, 29.9, 35.7, 37.2, 39.2, 68.4, 113.1, 124.3, 124.6, 130.6, 141.4, 165.3, 187.5.

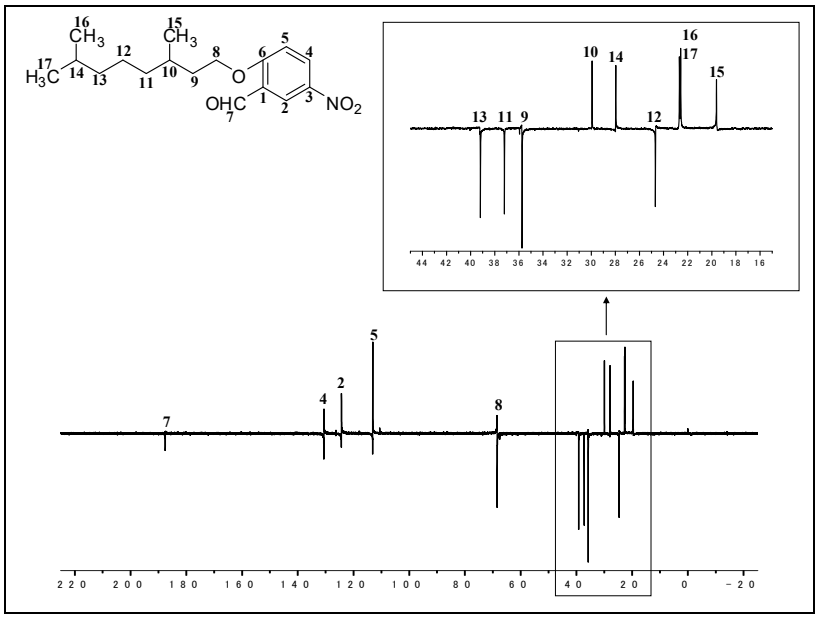


Figure S11. ^{13}C−NMR(DEPT−135) spectrum of 2-((*S*)-(−)-3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: $CDCl_3$.

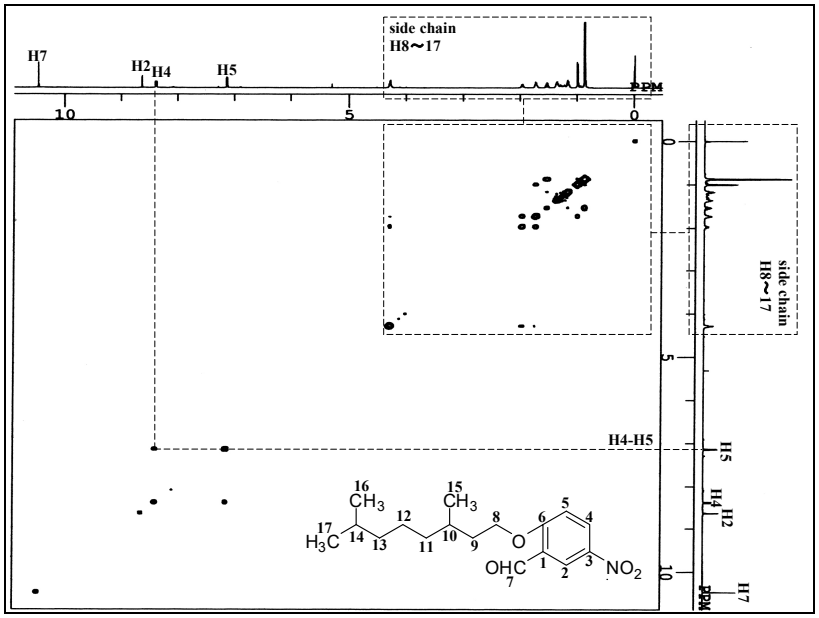


Figure S12. H,H−cosy spectrum of 2-((*S*)-(−)-3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: $CDCl_3$.

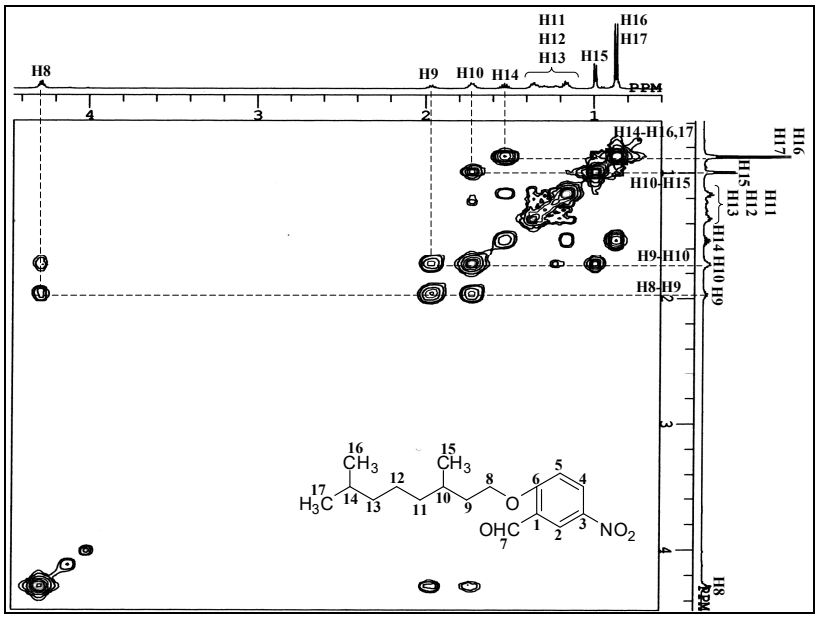


Figure S13. H,H−cosy spectrum of 2-(*S*)-(−)-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: $CDCl_3$. (expanded)

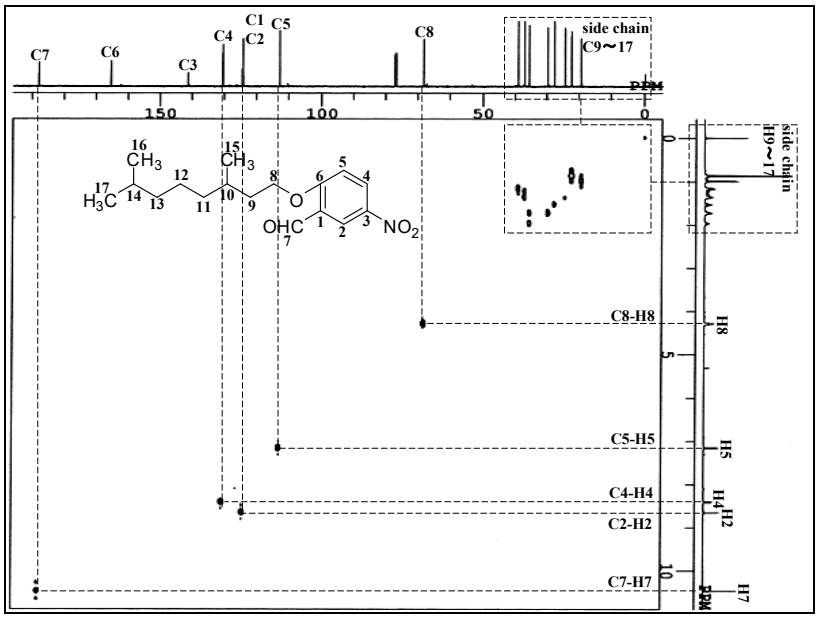


Figure S14. C,H−cosy spectrum of 2-((*S*)-(−)-3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: $CDCl_3$.

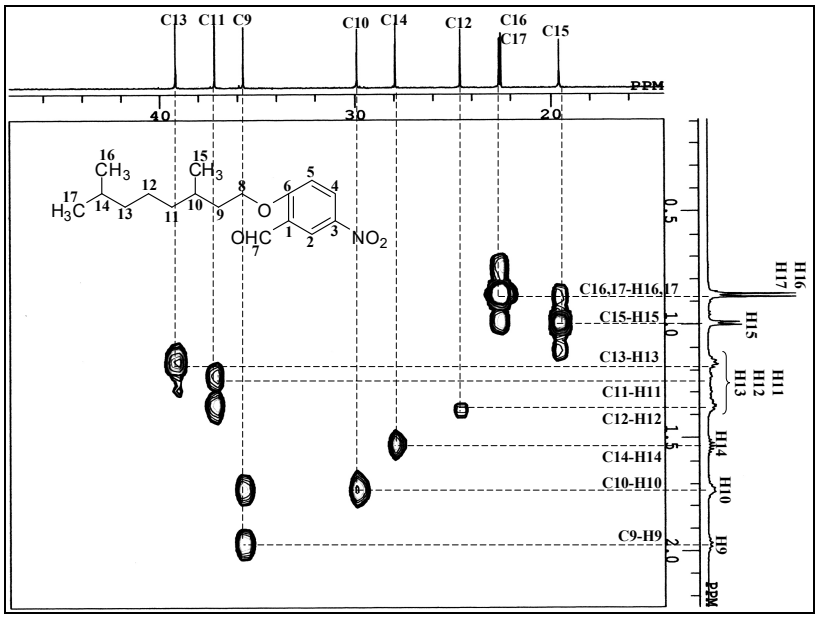


Figure S15. C,H−cosy spectrum of 2-((*S*)-(−)-3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: $CDCl_3$. (expanded)

2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde

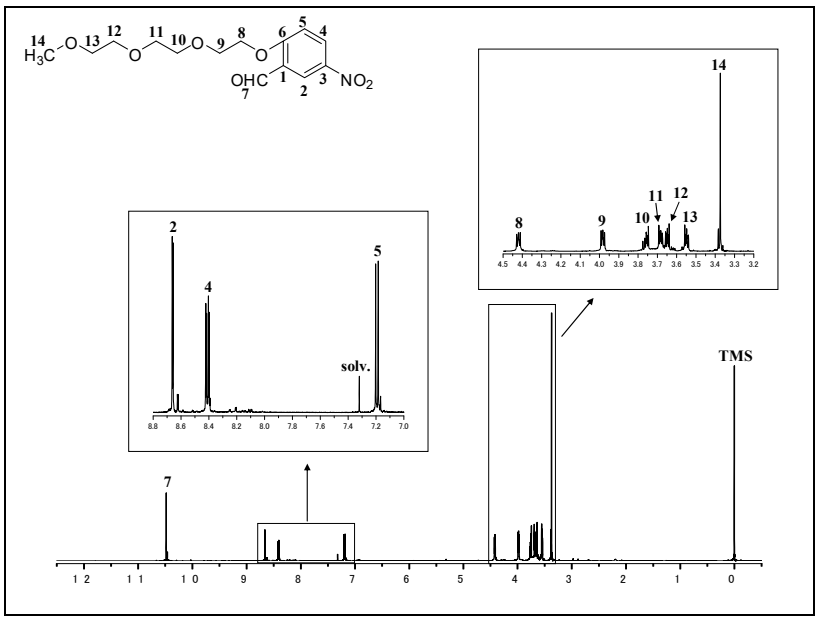


Figure S16. ^{1}H−NMR spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehydel; solvent: $CDCl_3$.

^{1}H−NMR(δ, ppm): 3.37(s,3H), 3.53−3.55(m,2H), 3.63−3.69(m,4H), 3.74−3.77(m,2H), 3.98(t,J=4.5,2H), 4.42(t,J=4.5Hz, 2H), 7.19(d,J=9.4Hz,1H), 8.41(d,J=6.4Hz,1H), 8.66(d,J=2.7Hz,1H), 10.48(s,1H).

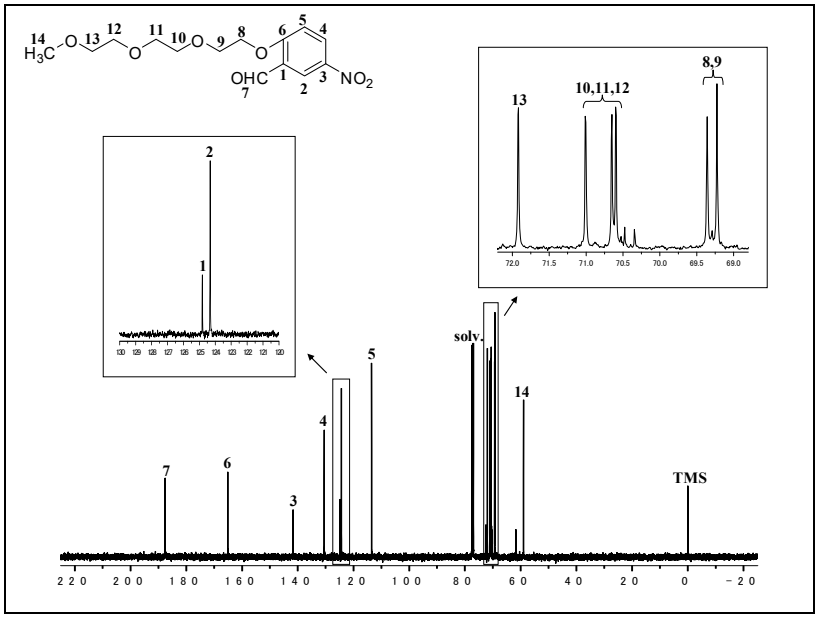


Figure S17. ^{13}C-NMR spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehydel; solvent: CDCl3, internal standard: TMS.

^{13}C-NMR (δ, ppm): 59.0, 69.2, 69.4, 70.6, 70.6, 71.0, 71.9, 113.5, 124.3, 124.8, 130.5, 141.7, 165.1, 187.6.

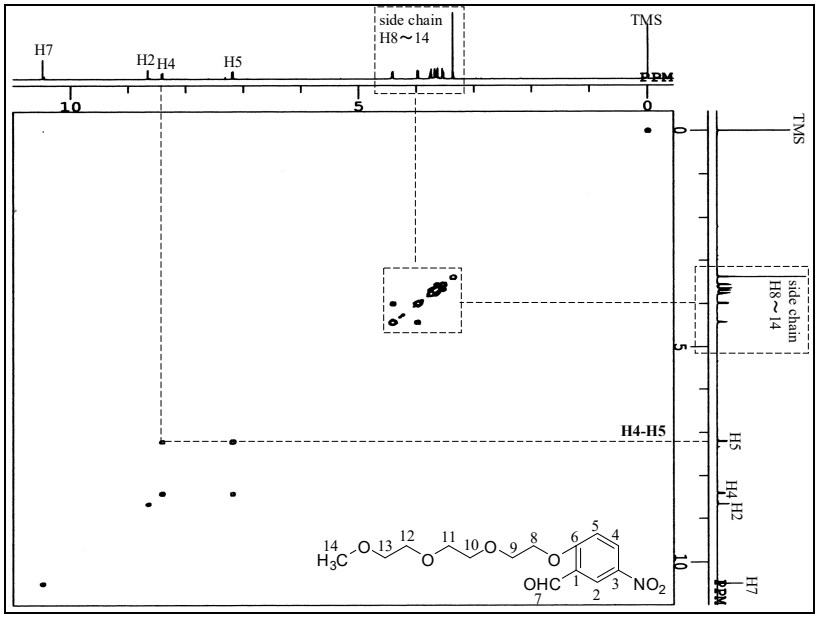


Figure S18. H,H−cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde; solvent: $CDCl_3$.

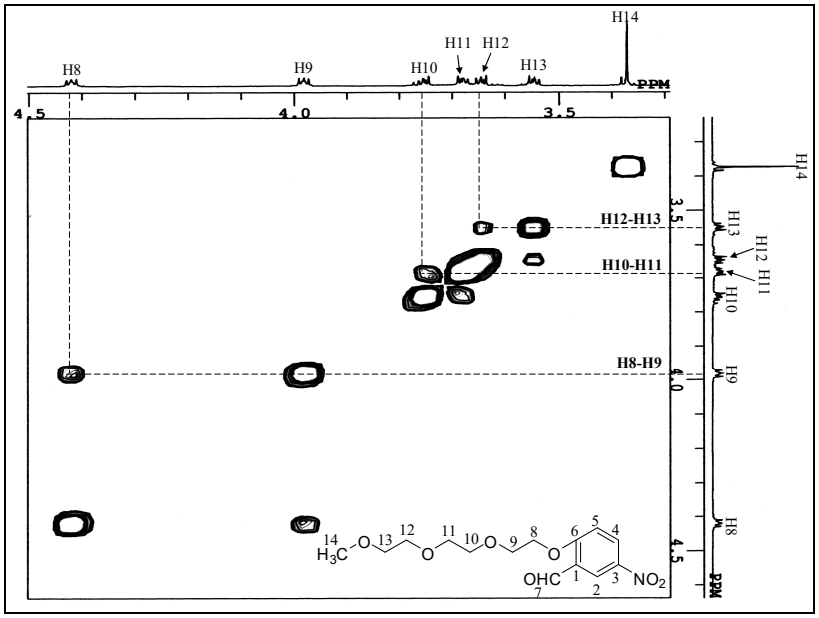


Figure S19. H,H−cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde; solvent: $CDCl_3$. (expanded)

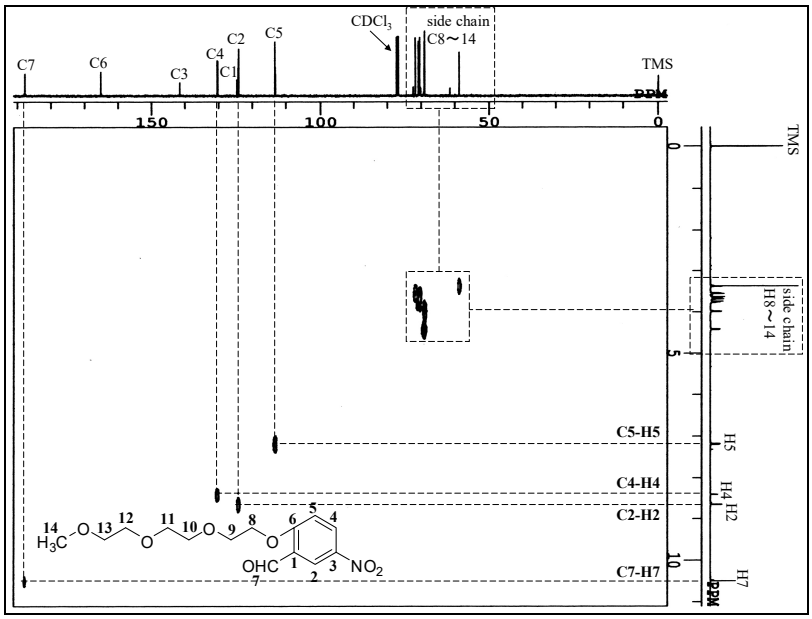


Figure S20. C,H−cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde; solvent: $CDCl_3$.

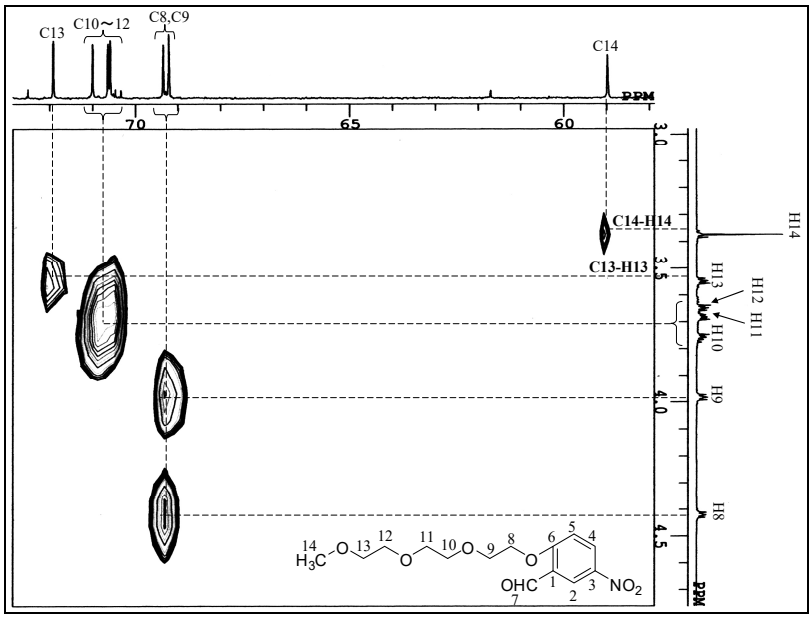


Figure S21. C,H−cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde; solvent: $CDCl_3$. (expanded)

2-Octyloxy-5-nitrobenzaldehyde diethyl acetal

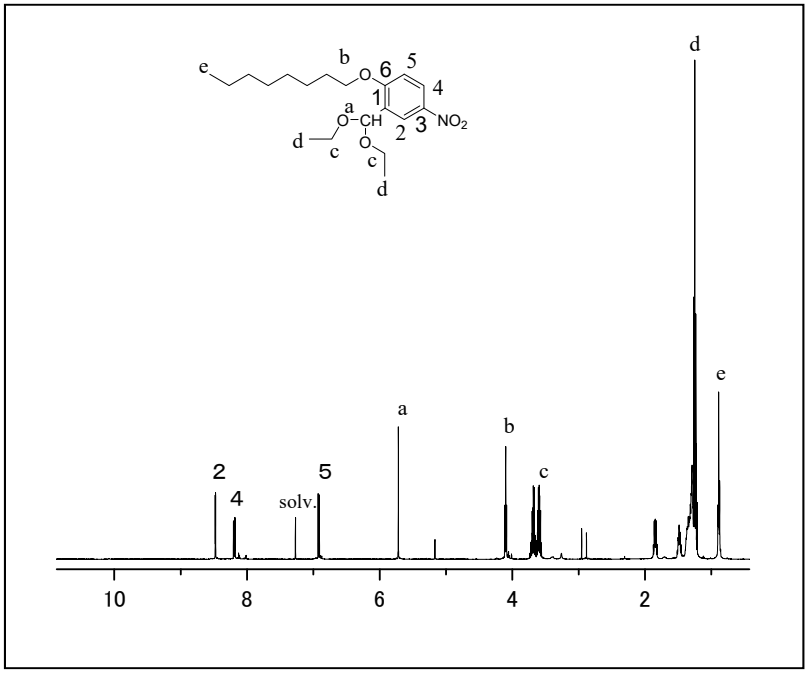


Figure S22. ^{1}H−NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde diethyl acetal; solvent: $CDCl_3$.

^{1}H−NMR (δ, ppm): 0.89(t,J=6.7Hz,3H,H−e), 1.25(t,J=7.0Hz,6H,H−d), 1.29(m,8H), 1.49(quin,J=7.6Hz,2H), 1.85(quin,J=7.0Hz,2H), 3.63(m,4H,H−c), 4.10(t,J=6.4Hz,2H,H−b), 5.72(s,1H,−CH−(acetal)), 6.91(d,J=8.9Hz,1H,H−5), 8.18(quar,J=6.1Hz,1H,H−4), 8.47(d,J=2.8Hz,1H,H−2)

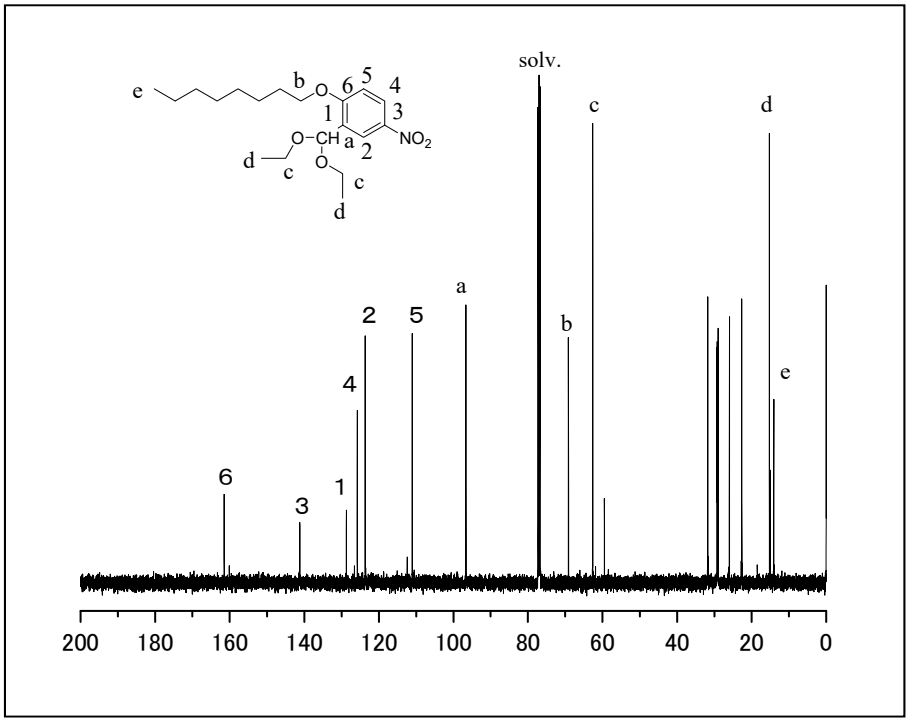


Figure S23. ^{13}C−NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde diethyl acetal; solvent: $CDCl_3$.
^{13}C−NMR (δ, ppm): 14.1(C−e), 15.2(C−d), 29.0, 29.2, 29.3, 31.8, 62.6(C−c), 69.1(C−b), 96.7(C−a), 111.1(C−5), 123.6(C−2), 125.8(C−4), 128.7(C−1), 141.2(C−3), 161.5(C−6).

2-((*S*)-(−)-3,7-Dimethyloctyloxy)-5-nitrobenzaldehyde diethyl acetal

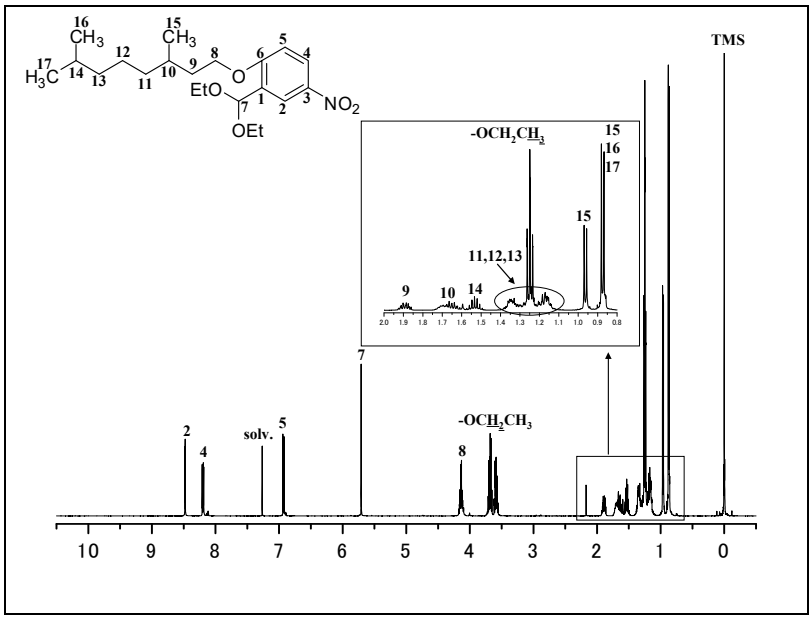


Figure S24. ^{1}H−NMR spectrum of 2-((*S*)-(−)-3,7-dimethyloctyloxy)-5-nitrobenzaldehyde diethyl acetal; solvent: $CDCl_3$.

^{1}H−NMR (δ, ppm): 0.87(d,J=6.7Hz,6H), 0.96(d,J=6.4Hz,3H), 1.14−1.36(m,6H), 1.24(t,J=7.0Hz,6H), 1.49−1.73(m,3H), 1.86−1.92(m,1H), 3.56−3.71(m,4H), 4.11−4.15(m,2H), 6.93(d,J=9.1Hz,1H), 8.19(d,J=9.1Hz,1H), 8.48(d,J=2.7Hz,1H).

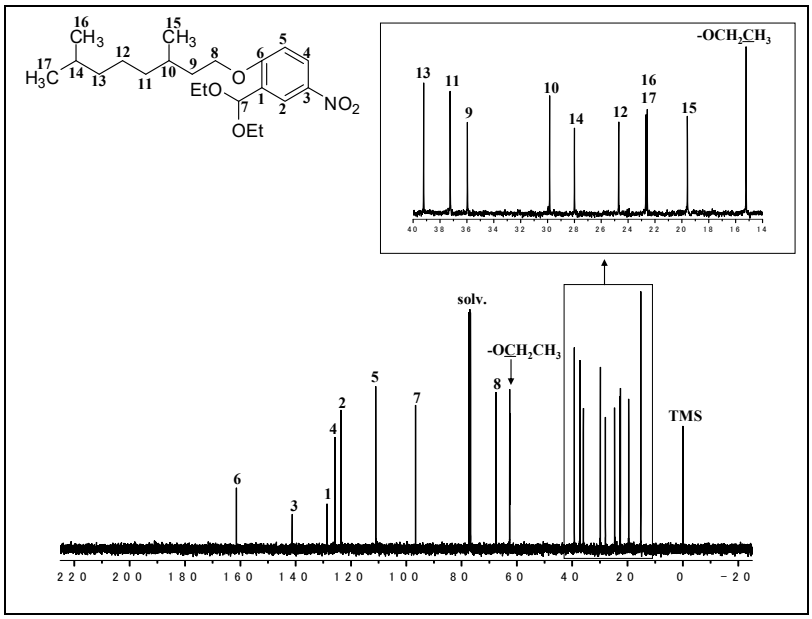


Figure S25. ^{13}C−NMR spectrum of 2-((*S*)-(−)-3,7-dimethyloctyloxy)-5-nitrobenzaldehyde diethyl acetal; solvent: $CDCl_3$.

^{13}C−NMR (δ, ppm): 15.2, 19.6, 22.6, 22.7, 24.7, 278.0, 29.8, 36.0, 37.2, 39.2, 62.6, 67.5, 96.7, 111.0, 123.6, 125.8, 128.7, 141.2, 161.4.

2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde diethyl acetal

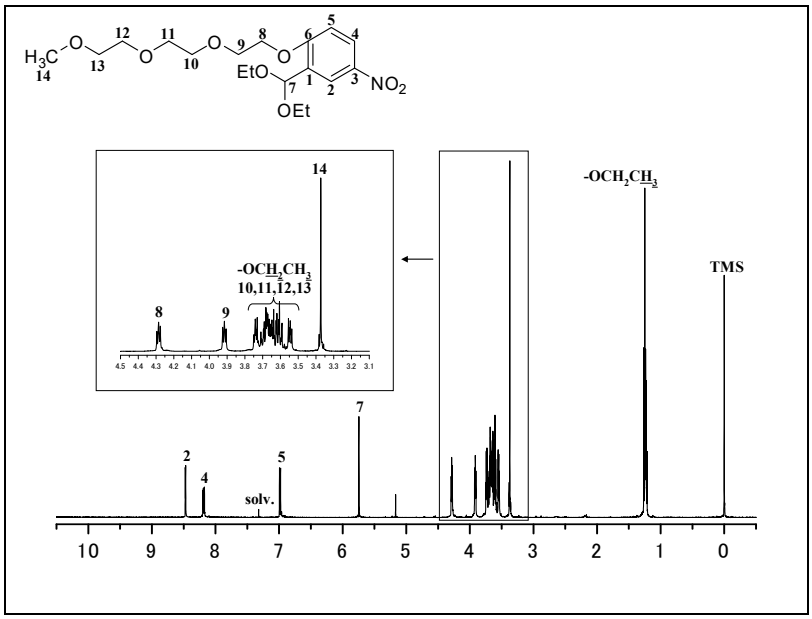


Figure S26. ^{1}H−NMR of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde diethylacetal; solvent: $CDCl_3$.
^{1}H−NMR (δ, ppm): 1.21(t,J=7.0Hz,6H), 3.37(s,3H), 3.53−3.55(m,2H), 3.59−3.71(m,8H), 3.73−3.74(m,2H), 3.91(t,J= 4.8Hz,2H), 4.28(t,J=4.5Hz,2H), 5.74(s,1H), 6.98(d,J=9.1Hz,1H), 8.10(d,J=6.1Hz,1H), 8.47(d,J= 3.0Hz,1H).

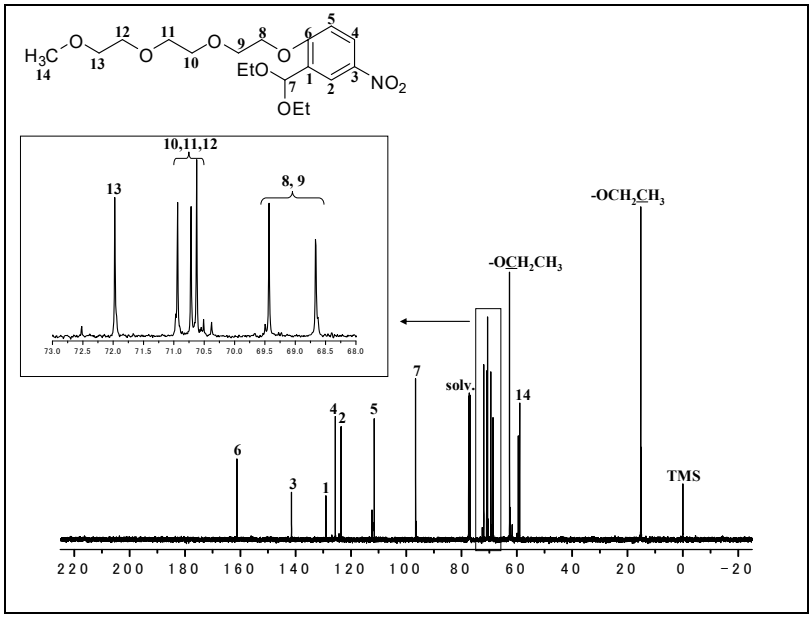


Figure S27. ^{13}C−NMR of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde diethylacetal; solvent: $CDCl_3$.
^{13}C−NMR (δ, ppm): 15.2, 59.0, 62.7, 68.7, 69.4, 70.6, 70.7, 70.9, 72.0, 96.6, 111.6, 123.6, 125.6, 129.1, 141.5, 161.2.

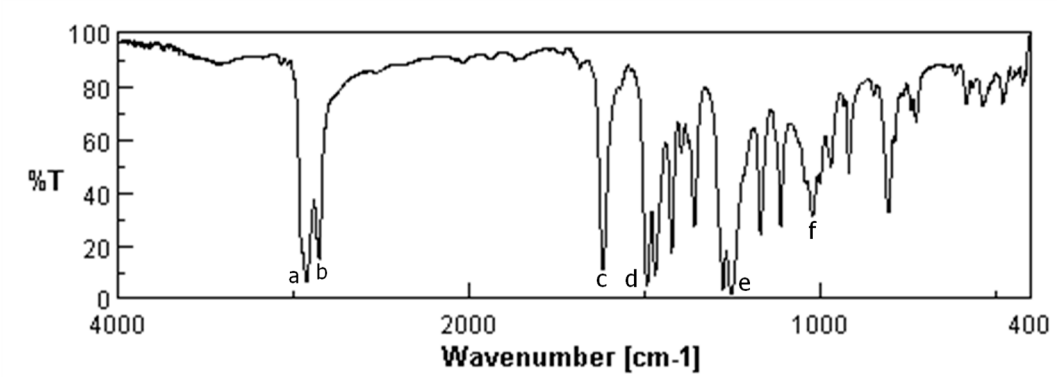


Figure S28. FT−IR spectrum of hexakis(2-octyloxy-1,5-phenyleneimine) macrocycle OcO−Cm6.

FT−IR(KBr, cm^{-1}): 2925 (νC−H,CH_3), 2852 (νC−H,CH_2), 1618 (νC=N), 1492, 1253, 1021.

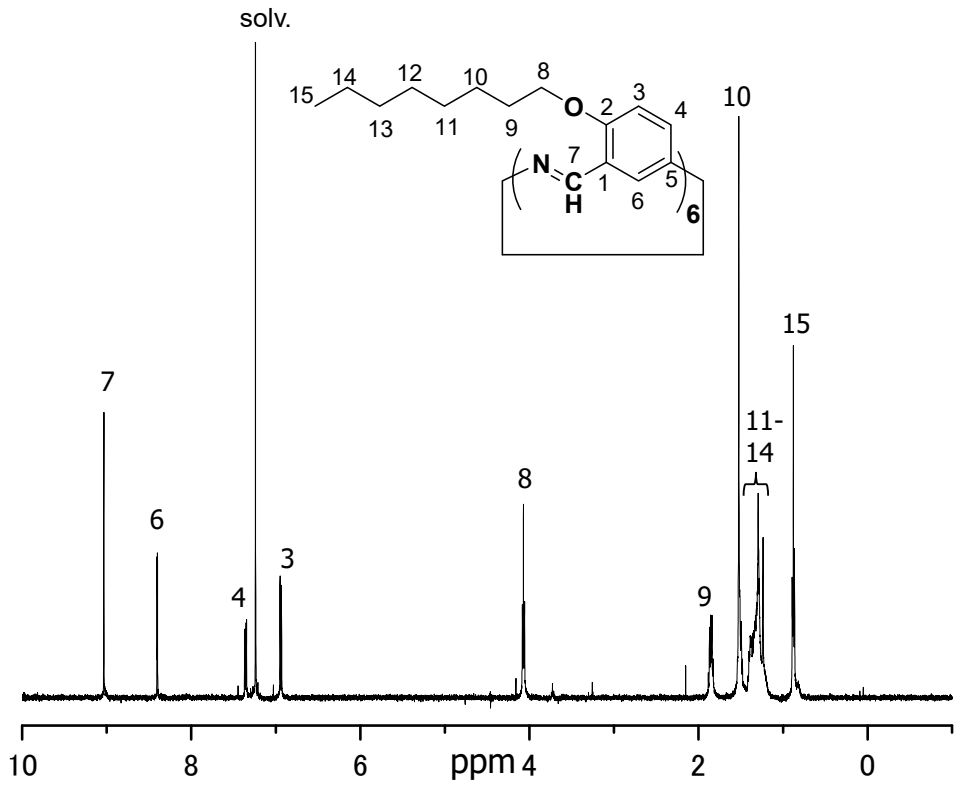


Figure S29. ^{1}H−NMR spectrum of hexakis(2-octyloxy-1,5-phenyleneimine) macrocycle (OcO−Cm6) in $CDCl_3$.

^{1}H-NMR(δ, ppm): 0.83(t,J=7.0Hz,3H,H-15), 1.24(m,8H, H-11,12,13,14), 1.48(quin,J=10.4Hz,2H,H-10), 1.81(quin,J=8.0Hz,2H,H-9), 4.02(t,J=6.7Hz,2H,H-8), 6.90(d,J=8.9Hz,1H,H-3), 7.30(quar,J=2.7Hz,1H,H-4), 8.35(d,J=2.7Hz,1H,H-6), 8.98(s,1H,H-7).

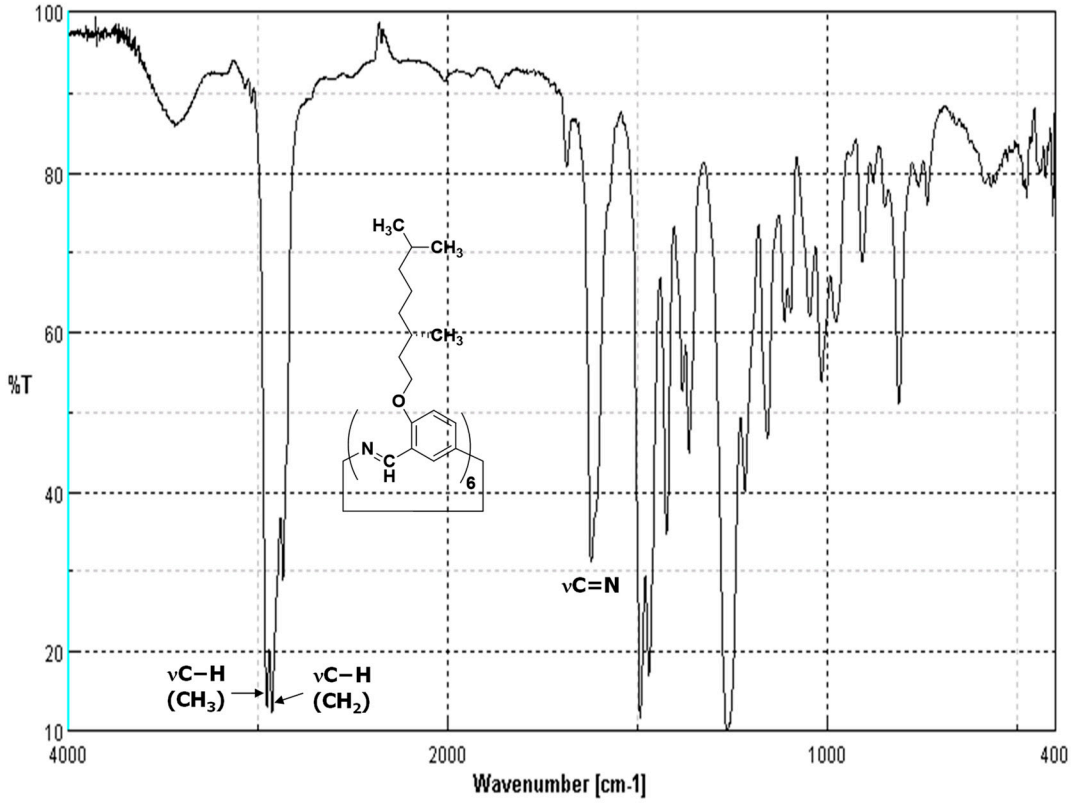


Figure S30. FT-IR spectrum of hexakis(2-((*S*)-(−)-3,7-dimethyloctyloxy)-1,5-phenyleneimine) macrocycle ((−)BCO−Cm6).

FT−IR(KBr, cm^{-1}): 2925(νC−H,CH_3), 2869(νC−H,CH_2), 1623(νCH=N), 1494, 1383, 1364, 1265, 1016.

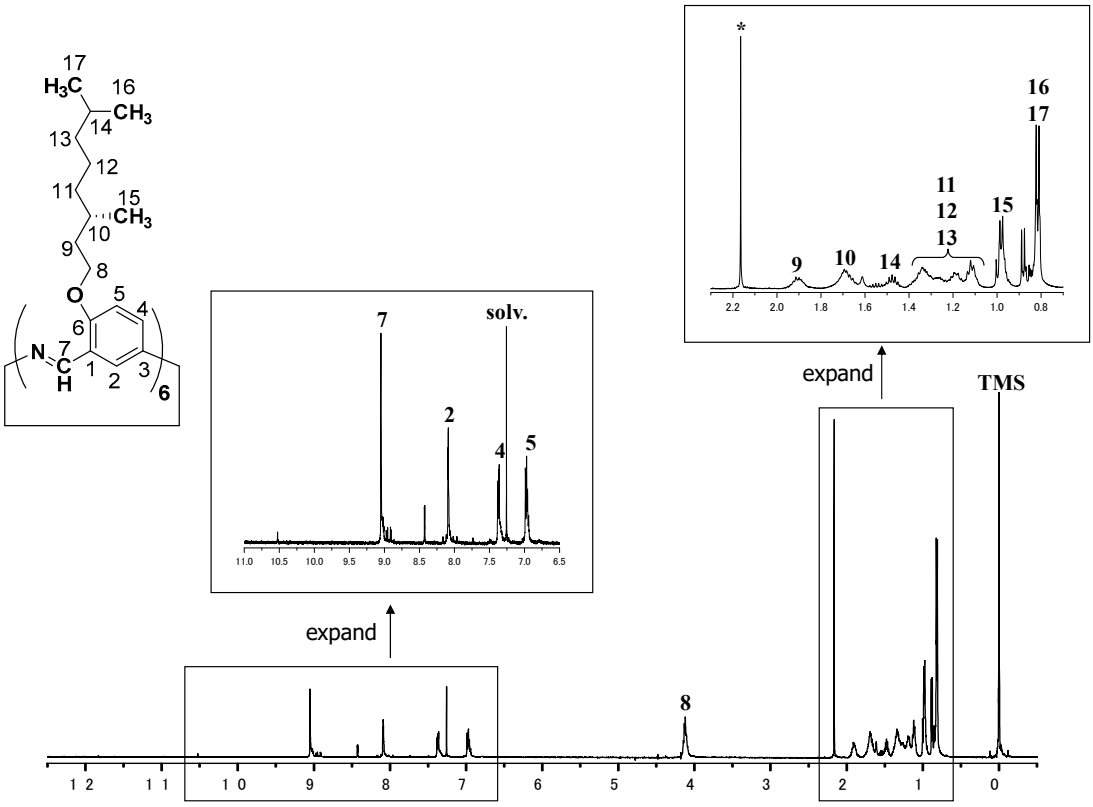


Figure S31. ^{1}H−NMR spectrum of hexakis(2-((*S*)-(−)-3,7-dimethyloctyloxy)-1,5-phenyleneimine) macrocycle ((−)BCO−Cm6) in $CDCl_3$.

^{1}H−NMR(δ, ppm): 0.82(d,J=6.7Hz,6H,H−16,17), 0.98(d,J=6.4Hz,3H,H−15), 1.08−1.39(m,6H,H−11,12,13), 1.45−1.72(m,2H,H−10,14), 1.87−1.93(m,2H,H−9), 4.08−4.14(m,2H,H−8), 6.98(d,J=8.8Hz,1H,H−3), 7.37(d,J=8.8Hz,1H,H−4), 8.09(d,J=2.7Hz,1H,H−6), 9.05(s,1H,H−7).

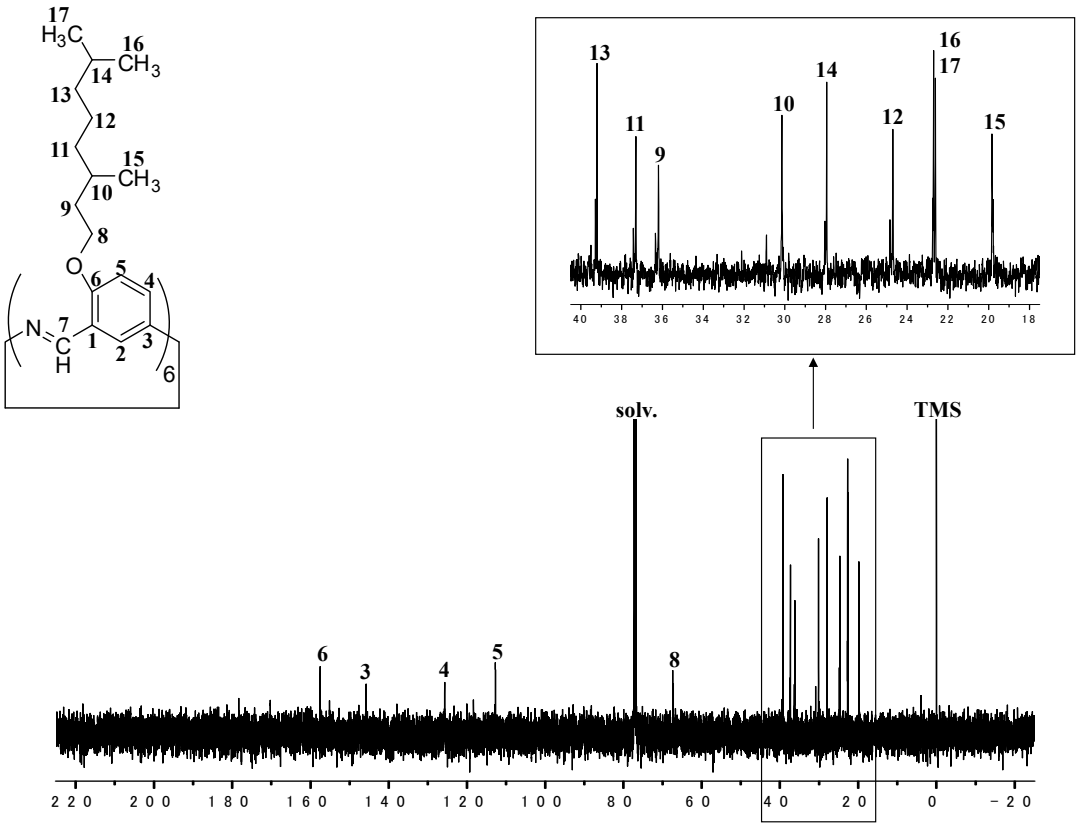


Figure S32. ^{13}C−NMR spectrum of hexakis(2-((*S*)-(−)-3,7-dimethyloctyloxy)-1,5-phenyleneimine) macrocycle ((−)BCO−Cm6) in $CDCl_3$.

^{13}C−NMR(δ, ppm): 19.8(C−15), 22.6(C−17), 22.7(C−16), 24.7(C−12), 27.9(C−14), 30.1(C−10), 36.2(C−9), 37.3(C−11), 39.2(C−13), 67.4(C−8), 112.7(C−5), 125.7(C−4), 145.8(C−3), 157.5(C−6).