Supporting Information

Rim-Differentiated C_5-Symmetric Tiara-Pillar[5]arenes

Minjie Guo,[†] Xuemei Wang,[†] Caihong Zhan,[†] Paul Demay-Drouhard,[†] Wenjiao Li,[†] Ke Du,[†] Mark A. Olson,[†] Han Zuilhof,*[,†,‡,§] and Andrew C.-H. Sue*[,†]

[†]Institute for Molecular Design and Synthesis, School of Pharmaceutical Science & Technology, Health Science Platform, Tianjin University, 92 Weijin Road, Nankai District, Tianjin, 300072, People's Republic of China
[‡]Laboratory of Organic Chemistry, Wageningen University, Stippeneng 4, 6703 WE Wageningen, The Netherlands
[§]Department of Chemical and Materials Engineering, King Abdulaziz University, Jeddah, Saudi Arabia

* andrew.sue@tju.edu.cn
* han.zuilhof@wur.nl

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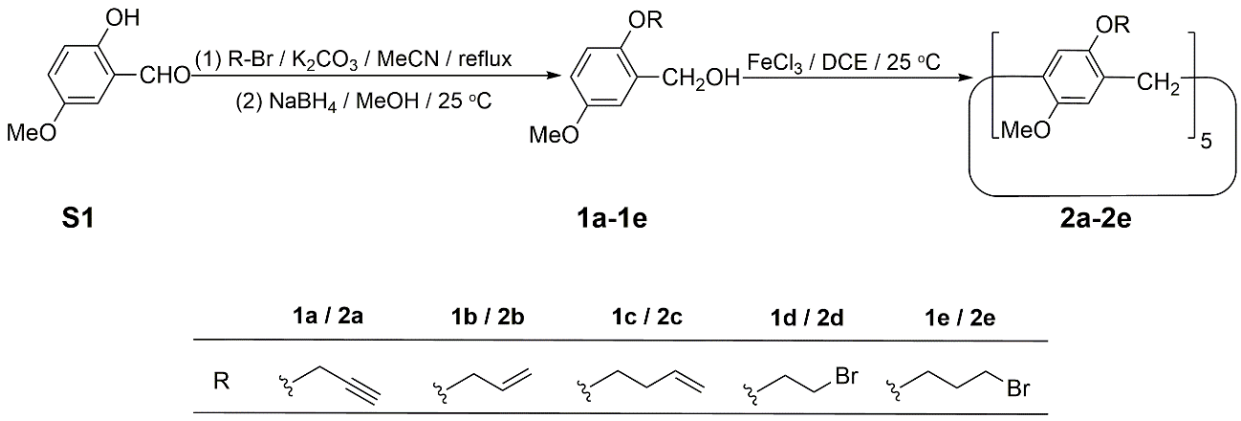
S1. Materials and General Methods

Starting materials, reagents, and solvents were purchased from commercial vendors and used as received, unless otherwise noted. All reactions were performed under an argon atmosphere and in dry solvents, unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets, precoated with silica gel GF_{254}. Flash column chromatography was performed over silica gel (200−300 mesh or 300−400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer at ambient temperature, unless otherwise noted. The chemical shifts are listed in ppm on the δ scale and coupling constants were recorded in Hertz (Hz). Chemical shifts are calibrated relative to the signals corresponding of the non-deuterated solvents ($CHCl_3$: δ 7.26 ppm). The following abbreviations were used for multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet or overlapping peaks; b, broad peaks. High resolution mass spectra (HRMS) were measured on a QTOF micro spectrometer. HPLC analyses were performed on an Agilent 1260 liquid chromatography system with an Agilent ZORBAX SB-C_{18} column (150 mm × 4.6 mm, 5 μm). Prep-HPLC was performed using a LC-6AD secondary (2 pumps) semi-preparative HPLC system (Shimadzu Technologies, Japan) with an Agilent ZORBAX SB-C_{18} PrepHT column (21.2 × 250 mm) (Agilent Technologies, USA).

S2. General Synthetic Procedures



Scheme S1. The syntheses of tiara-pillar[5]arenes **2a-2e** and their corresponding monomeric precursors **1a-1e**.

1a: To a solution of 2-hydroxy-5-methoxybenzaldehyde **S1** (2.0 g, 13.1 mmol) in MeCN (60 mL) was added K_2CO_3 (3.6 g, 26.2 mmol) followed by 3-bromoprop-1-yne (1.47 mL, 19.7 mmol). The reaction mixture was sealed and refluxed while being monitored by TLC. After **S1** was reacted completely, the reaction mixture was filtered to remove K_2CO_3 and then concentrated. The resulting residue was dissolved in MeOH (50 mL), to which $NaBH_4$ (250 mg, 6.5 mmol) was added. The solution was stirred at room temperature for 5 min and the solvent was then removed under reduced pressure. The residue was dissolved in H_2O (30 mL) and the aqueous solution was extracted with ethyl acetate (3 × 30 mL). The combined organic phase was dried (Na_2SO_4) and the solvent was removed under low pressure. The resulting crude product was purified by silica gel column chromatography using EtOAc/*n*-hexane as eluents (from 1:9 to 1:6) to obtain the product **1a** as a yellow oil (1.87 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (s, 1H), 6.92 (d, J = 3.6 Hz, 1H), 6.79 (m, 1H), 4.70 (d, J = 2.4 Hz, 2H), 4.68 (s, 2H), 3.78 (s, 3H), 2.51 (t, J = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.5, 149.4, 131.2, 114.8, 113.6, 113.1, 78.7, 75.6, 61.7, 56.9, 55.7. HRMS (ESI): calcd for $C_{11}H_{12}O_3Na$ $[M + Na]^+$ m/z = 215.0684; found m/z = 215.0678.

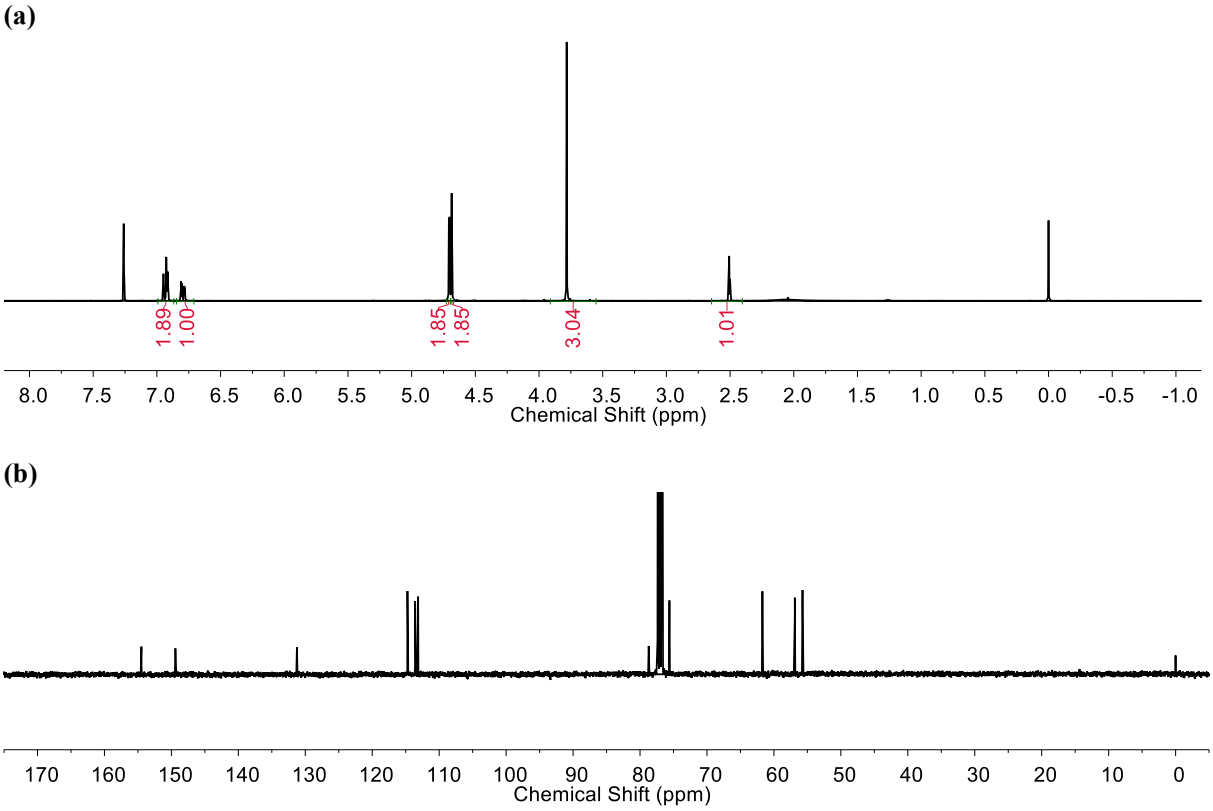


Figure S1. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of **1a** recorded in $CDCl_3$ at 298 K.

1b: To a slurry of **S1** (3.0 g, 20 mmol) and K_2CO_3 (4.1 g, 30 mmol) in MeCN (25 mL) was added 3-bromoprop-1-ene (2.2 mL, 30 mmol). The reaction mixture was sealed and refluxed overnight. Then more 3-bromoprop-1-ene (2.2 mL, 30 mmol) was added. After **S1** was reacted completely, the reaction mixture was filtered to remove K_2CO_3 and then concentrated. The resulting residue was dissolved in MeOH (100 mL), to which $NaBH_4$ (380 mg, 10 mmol) was added. The solution was stirred at room temperature for 5 min until TLC indicated the complete conversion from aldehyde to alcohol, and the solvent was then removed under reduced pressure. The crude product was purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (from 1:10 to 1:8 to 1:6) to obtained the product **1b** as a light yellow oil (3.3 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86–6.85 (d, J = 2.0 Hz, 1H), 6.81–6.75 (m, 2H), 6.08–6.01 (m, 1H), 5.41–5.38 (m, 1H), 5.29–5.27 (m, 1H), 4.69 (s, 2H), 4.54 (s, 2H), 3.77 (s, 3H), 2.42 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.8, 150.5, 133.3, 130.1, 117.5, 114.7, 113.0, 112.7, 69.5, 62.0, 55.8. HRMS (ESI): calcd for $C_{11}H_{14}O_3Na$ $[M + Na]^+$ m/z = 217.0841, found m/z = 217.0837.

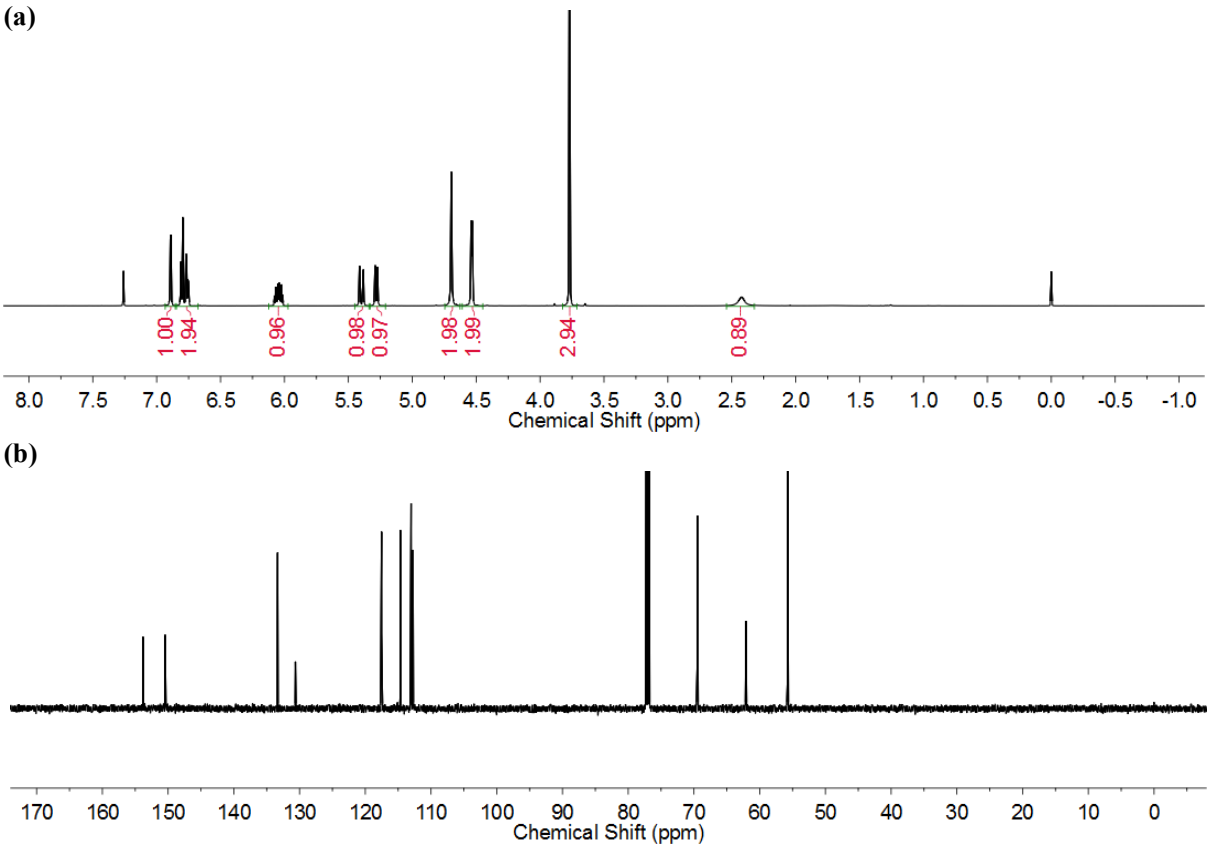


Figure S2. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of **1b** recorded in $CDCl_3$ at 298 K.

1c: To a slurry of **S1** (3.0 g, 20 mmol) and K_2CO_3 (4.1 g, 30 mmol) in MeCN (25 mL) was added 4-bromobut-1-ene (2.2 mL, 30 mmol). The mixture was sealed and refluxed overnight. Since TLC indicated the presence of starting material, NaI (0.9 g, 6 mmol) was added to the reaction mixture, which was refluxed for another 15 h before being filtered and concentrated. The resulting residue was dissolved in MeOH (50 mL), to which $NaBH_4$ (380 mg, 10 mmol) was added. The solution was stirred at room temperature for 10 min until TLC indicated the complete conversion from aldehyde to alcohol, and the solvent was then removed under reduced pressure. The crude product was purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (from 1:10 to 1:6) to obtained the product **1c** as a yellow oil (3.3 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86–6.85 (d, J = 2.0 Hz, 1H), 6.80–6.75 (m, 2H), 5.92–5.85 (m, 1H), 5.20–5.12 (m, 2H), 4.64 (s, 2H), 4.04–4.02 (t, J = 4.2 Hz, 2H), 3.76 (s, 3H), 2.56–2.53 (m, 2H), 2.40 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.7, 150.9, 134.7, 130.4, 117.3, 114.8, 113.0, 112.2, 67.4, 62.4, 55.8, 33.9. HRMS (ESI): calcd for $C_{12}H_{16}O_3Na$ $[M + Na]^+$ m/z = 231.0997, found m/z = 231.1000.

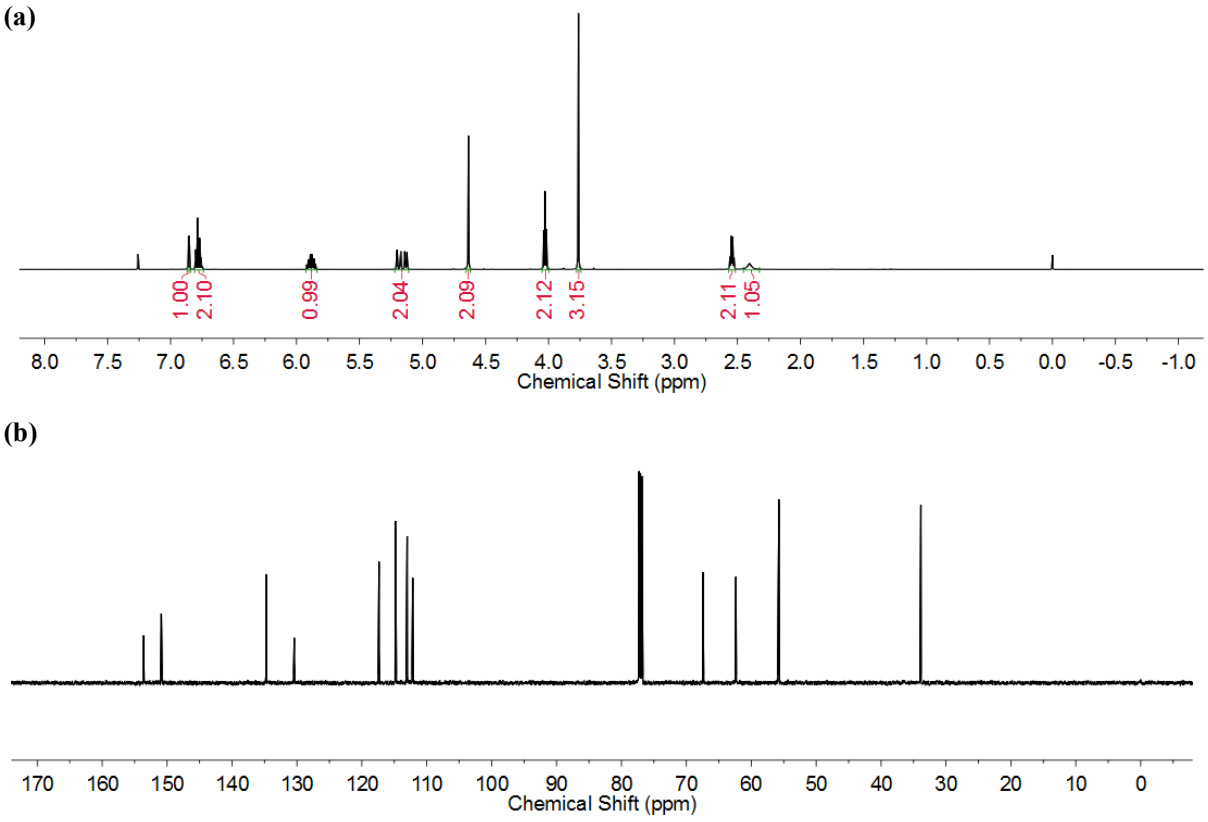


Figure S3. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of **1c** recorded in $CDCl_3$ at 298 K.

1d: To a slurry of **S1** (3.0 g, 20 mmol) and K_2CO_3 (4.1 g, 30 mmol) in MeCN (25 mL) was added 1,2-dibromoethane (5.6 g, 30 mmol). The reaction mixture was sealed and refluxed for 12 h. The reaction mixture was filtered to remove K_2CO_3 and then concentrated. The resulting residue was dissolved in MeOH (30 mL), to which $NaBH_4$ (380 mg, 10 mmol) was added. The solution was stirred at room temperature for 10 min until TLC indicated the complete conversion from aldehyde to alcohol, and the solvent was then removed under reduced pressure. The crude product purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (1:4) to provide the product **1d** as a light brown oil (3.6 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90–6.89 (d, J = 2.0 Hz, 1H), 6.78–6.75 (m, 2H), 4.68 (s, 2H), 4.30–4.28 (t, J = 2.8 Hz, 2H), 3.77 (s, 3H), 3.67–3.65 (t, J = 2.8 Hz, 2H), 2.47 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.2, 149.9, 131.1, 77.5, 77.2, 76.9, 68.5, 61.6, 55.8, 30.1. HRMS (ESI): calcd for $C_{10}H_{13}O_3BrNa$ $[M + Na]^+$ m/z = 282.9946; found m/z = 282.9932.

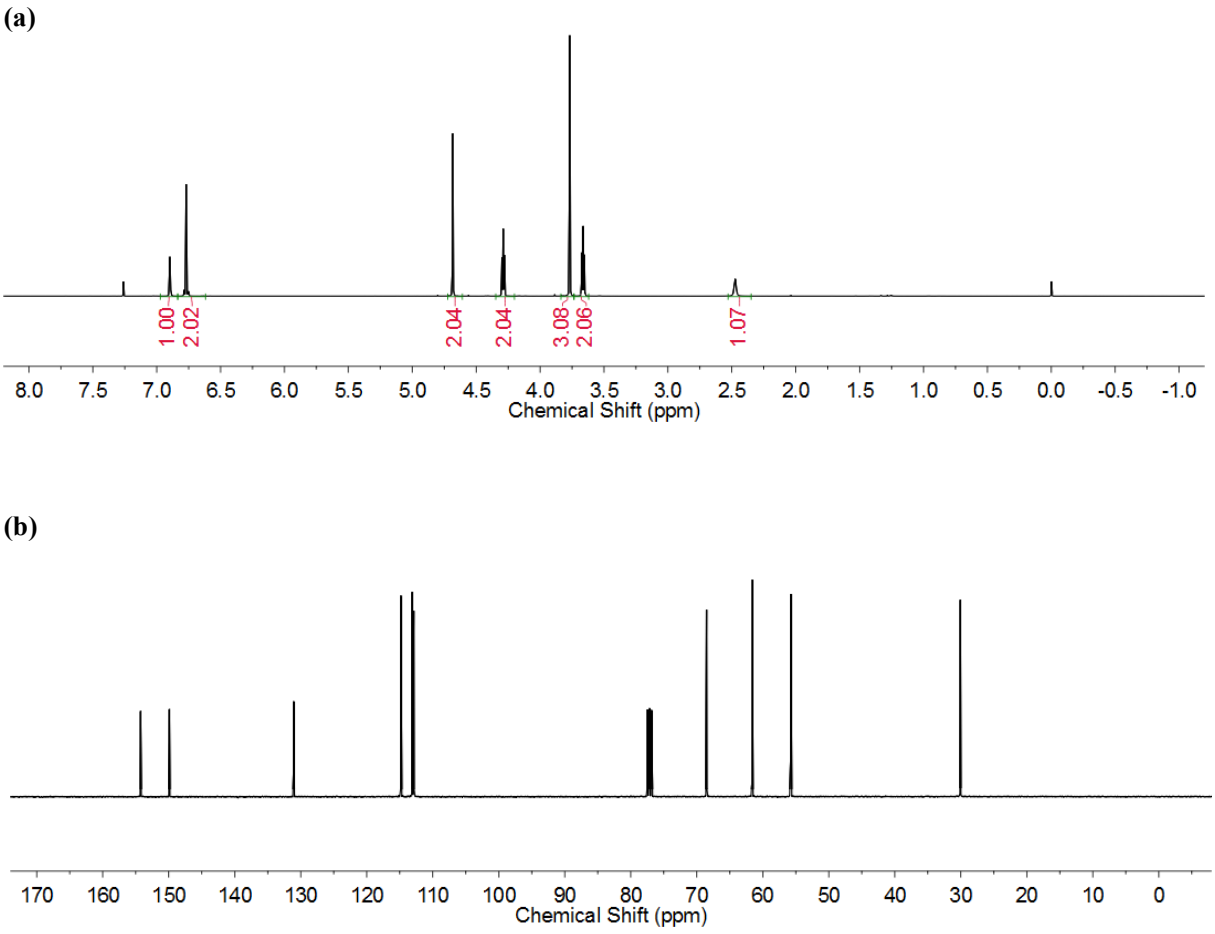


Figure S4. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of **1d** recorded in $CDCl_3$ at 298 K.

1e: To a slurry of **S1** (3.0 g, 20 mmol) and K_2CO_3 (4.1 g, 30 mmol) in MeCN (25 mL) was added 1,3-dibromopropane (6.0 g, 30 mmol). The mixture was sealed and refluxed for 15 h. The reaction mixture was filtered to remove K_2CO_3 and then concentrated. The resulting residue was dissolved in MeOH (30 mL), to which $NaBH_4$ (380 mg, 10 mmol) was added. The solution was stirred at room temperature for 10 min until TLC indicated the complete conversion from aldehyde to alcohol, and the solvent was then removed under reduced pressure. The resulting crude product was purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (1:8) to obtain the product **1e** as a light brown oil (4.5 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91–6.90 (d, J = 2.0 Hz, 1H), 6.84–6.76 (m, 2H), 4.66 (s, 2H), 4.12–4.09 (t, J = 2.8 Hz, 2H), 3.77 (s, 3H), 3.61–3.58 (t, J = 2.8 Hz, 2H), 2.35–2.29 (m, 2H), 2.26 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9, 150.3, 130.6, 114.5, 113.0, 112.6, 66.2, 61.4, 55.8, 32.4, 29.7. HRMS (ESI): calcd for $C_{11}H_{15}O_3BrNa$ $[M + Na]^+$ m/z = 297.0102, found m/z = 297.0103.

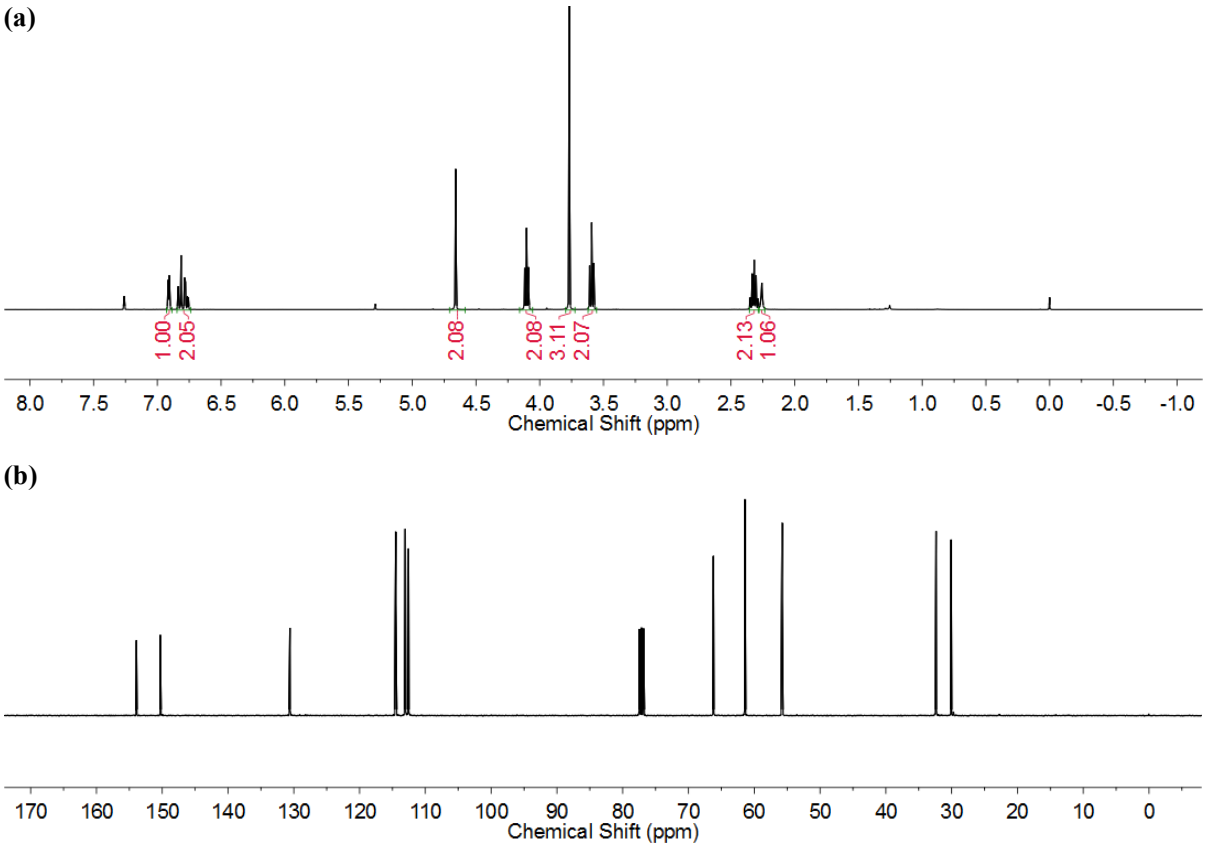


Figure S5. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of **1e** recorded in $CDCl_3$ at 298 K.

(Propargyl)$_5$-tiara-pillar[5]arene **2a**: To a stirred suspension of **1a** (194 mg, 1.00 mmol) in 1,2-dichloroethane (10 mL) was added $FeCl_3$ (17 mg, 0.10 mmol). The reaction mixture was stirred at 25 °C for 4 h before MeOH (2 mL) was added to quench the reaction. The solvent was removed under reduced pressure to yield a crude product, which was purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (from 1:15 to 1:10) to provide a mixture of the product **2a** together with the other three constitutional isomers as a light yellow solid (63 mg, 38%). R_f = 0.26 (EtOAc/*n*-hexane = 1:4). Pure (propargyl)$_5$-tiara-pillar[5]arene **2a** can be crystallized by slow vapor diffusion of hexane into ethyl acetate solution of the isolated mixture. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.82 (s, 5H), 6.75 (s, 5H), 4.45–4.44 (d, J = 1.2 Hz, 10H), 3.79 (s, 10H), 3.72 (s, 15H), 2.14 (s, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.2, 148.8, 129.0, 128.2, 115.6, 114.0, 79.3, 74.7, 56.5, 55.9, 29.7. HRMS (ESI): calcd for $C_{55}H_{50}O_{10}Na$ $[M + Na]^+$ m/z = 893.3302, found m/z = 893.3251.

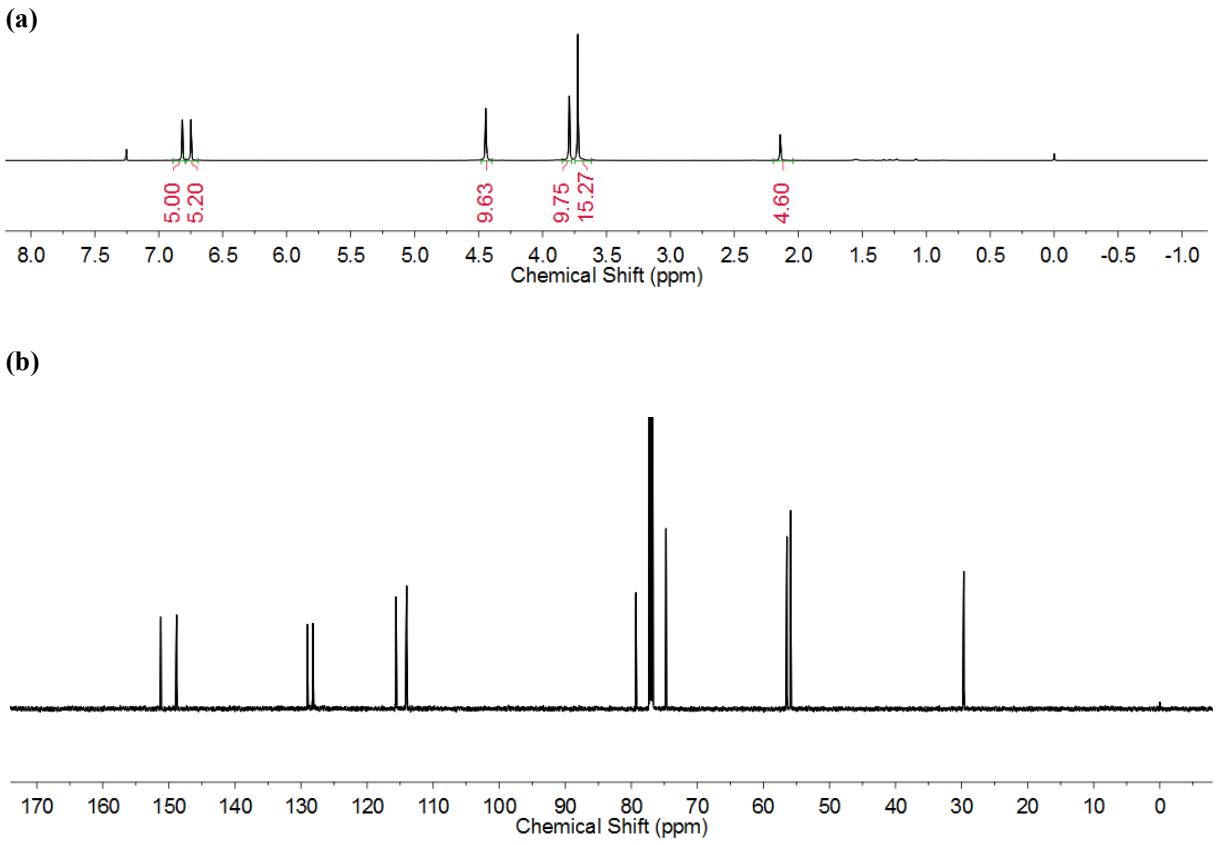


Figure S6. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of (propargyl)$_5$-tiara-pillar[5]arene **2a** recorded in $CDCl_3$ at 298 K.

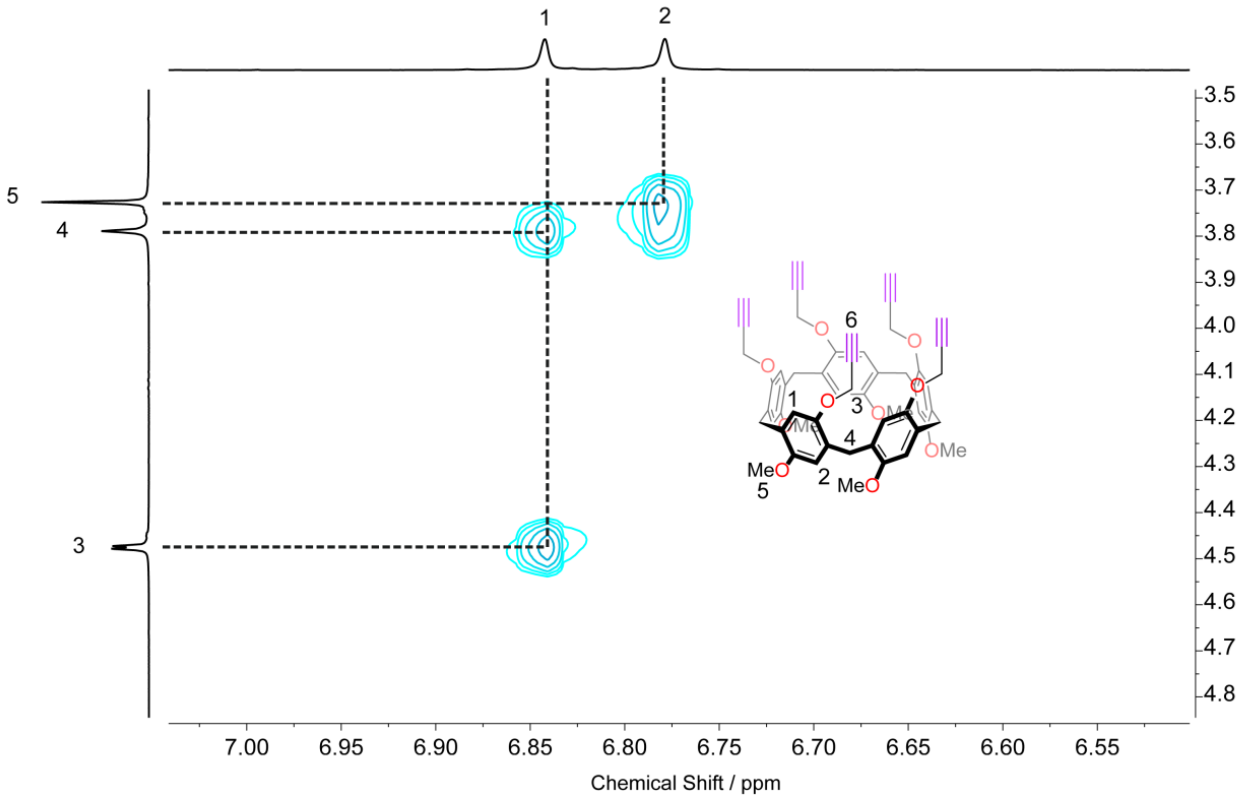


Figure S7. NOESY spectrum (400 MHz) of **2a** recorded in $CDCl_3$ at 298 K.

Conventional statistical synthesis protocol for **(**propargyl)$_5$-tiara-pillar[5]arene **2a**: To a stirred suspension of 4-methoxy-propargyloxy benzene[S1] (500 mg, 3.08 mmol) in 1,2-dichloroethane (30 mL) was added paraformaldehyde (110 mg, 3.69 mmol) followed by trifluoroacetic acid (1.5 mL). The mixture was heated at 85 °C for 3 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica-gel (200-300 mesh) using EtOAc/*n*-hexane as eluents (from 1:7 to 1:5) to obtain the mixtures of four (propargyl)$_5$-pillar[5]arene constitutional isomers as a white yellow solid (420 mg, 79%). R_f = 0.26 (EtOAc/*n*-hexane = 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85-6.70 (m, 10H), 4.43-4.41 (m, 10H), 3.78-3.79 (m, 10H), 3.73-3.71 (s, 15H), 2.14-2.05 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.12, 151.09, 151.06, 151.03, 148.76, 148.73, 148.68, 148.63, 129.06, 129.01, 128.56, 127.99, 115.44, 115.40, 115.38, 114.17, 114.14, 113.84, 113.81, 79.13, 79.10, 79.06, 78.94, 74.66, 74.58, 74.46, 74.43, 56.35, 56.33, 56.30, 55.82, 55.77, 55.74, 55.70, 30.91, 29.66, 29.52, 29.41, 28.29.

(Allyl)$_5$-tiara-pillar[5]arene **2b**: To a stirred suspension of **1b** (194 mg, 1.00 mmol) in 1,2-dichloroethane (10 mL) was added $FeCl_3$ (17 mg, 0.10 mmol). The reaction mixture was stirred at 25 °C for 8 h before MeOH (2 mL) was added to quench the reaction. The solvent was removed under reduced pressure to yield a crude product, which was purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (from 1:15 to 1:10) to obtain the product **2b** as a light yellow solid (28 mg, 16%). R_f = 0.3 (EtOAc/*n*-hexane = 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.68 (s, 5H), 6.59 (s, 5H), 5.56–5.46 (m, 10H), 4.94–4.90 (m, 10H), 4.71–4.68 (m, 15H), 4.13–4.12 (m, 10H), 3.71 (s, 10H), 3.64 (s, 15H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.2, 148.8, 129.0, 128.2, 115.6, 114.0, 79.3, 74.7, 56.5, 55.9, 29.7. HRMS (ESI): calcd for $C_{55}H_{60}O_{10}Na$ $[M + Na]^+$ *m*/*z* = 903.4084, found *m*/*z* = 903.4087.

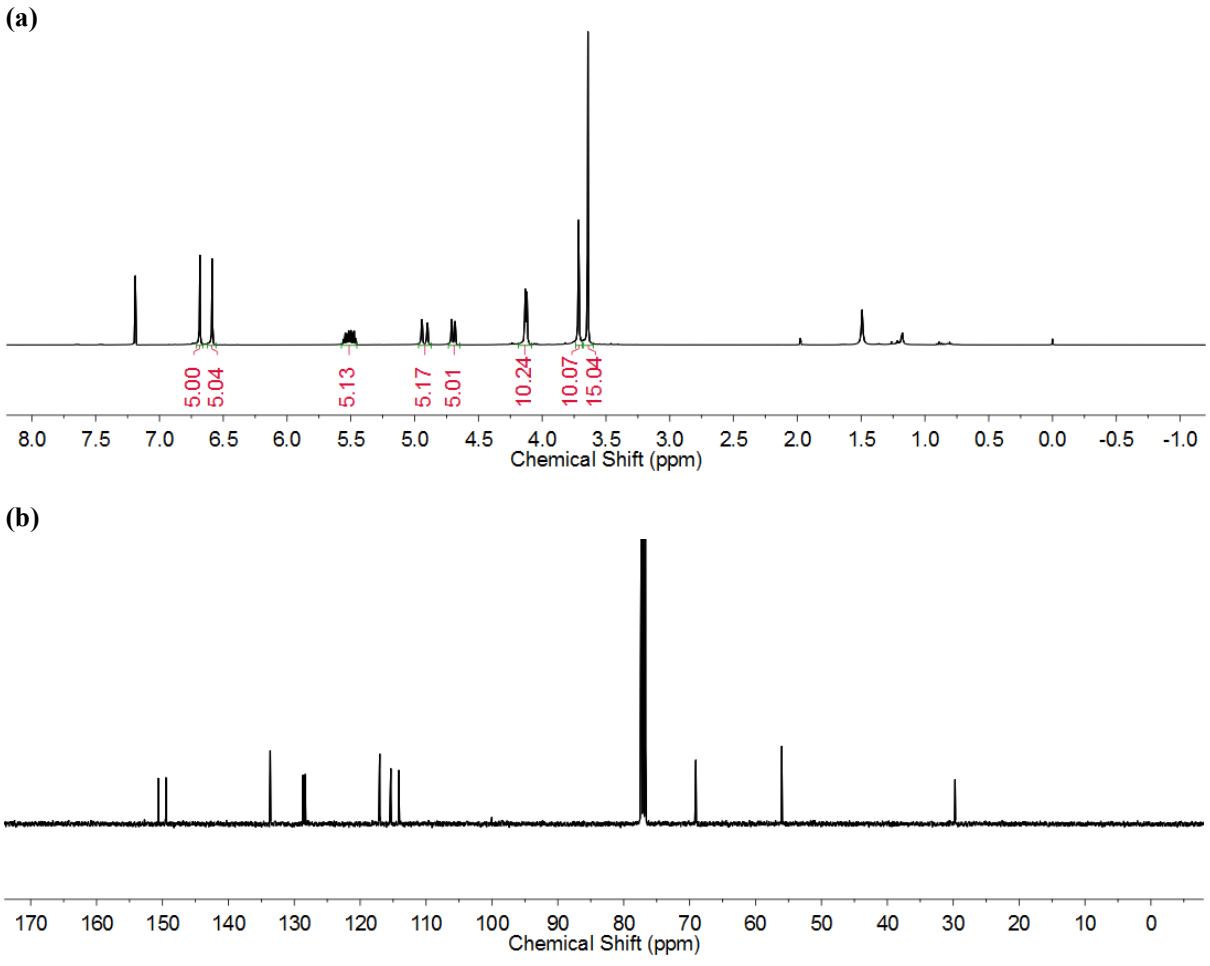


Figure S8. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of (allyl)$_5$-tiara-pillar[5]arene **2b** recorded in $CDCl_3$ at 298 K.

(Homoallyl)$_5$-tiara-pillar[5]arene **2c:** To a stirred suspension of **1c** (416 mg, 2.00 mmol) in 1,2-dichloroethane (20 mL) was added $FeCl_3$ (33 mg, 0.20 mmol). The mixture was stirred at 25 °C for 8 h before MeOH (2 mL) was added to quench the reaction. The solvent was removed under reduced pressure to yield a crude product, which was purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (from 1/20 to 1/15) to provide the product **2c** as a white yellow solid (64 mg, 18%). R_f = 0.3 (EtOAc/*n*-hexane = 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (s, 5H), 6.77 (s, 5H), 5.96–5.86 (m, 5H), 5.15–5.04 (m, 10H), 3.90–3.86 (m, 10H), 3.76 (s, 10H), 3.67 (s, 15H), 2.53–2.48 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.8, 149.9, 135.0, 128.4, 128.2, 116.7, 115.2, 114.0, 67.8, 55.8, 34.3, 29.5. HRMS (ESI): calcd for $C_{60}H_{70}O_{10}Na$ $[M + Na]^+$ m/z = 973.4867; found m/z = 973.4819.

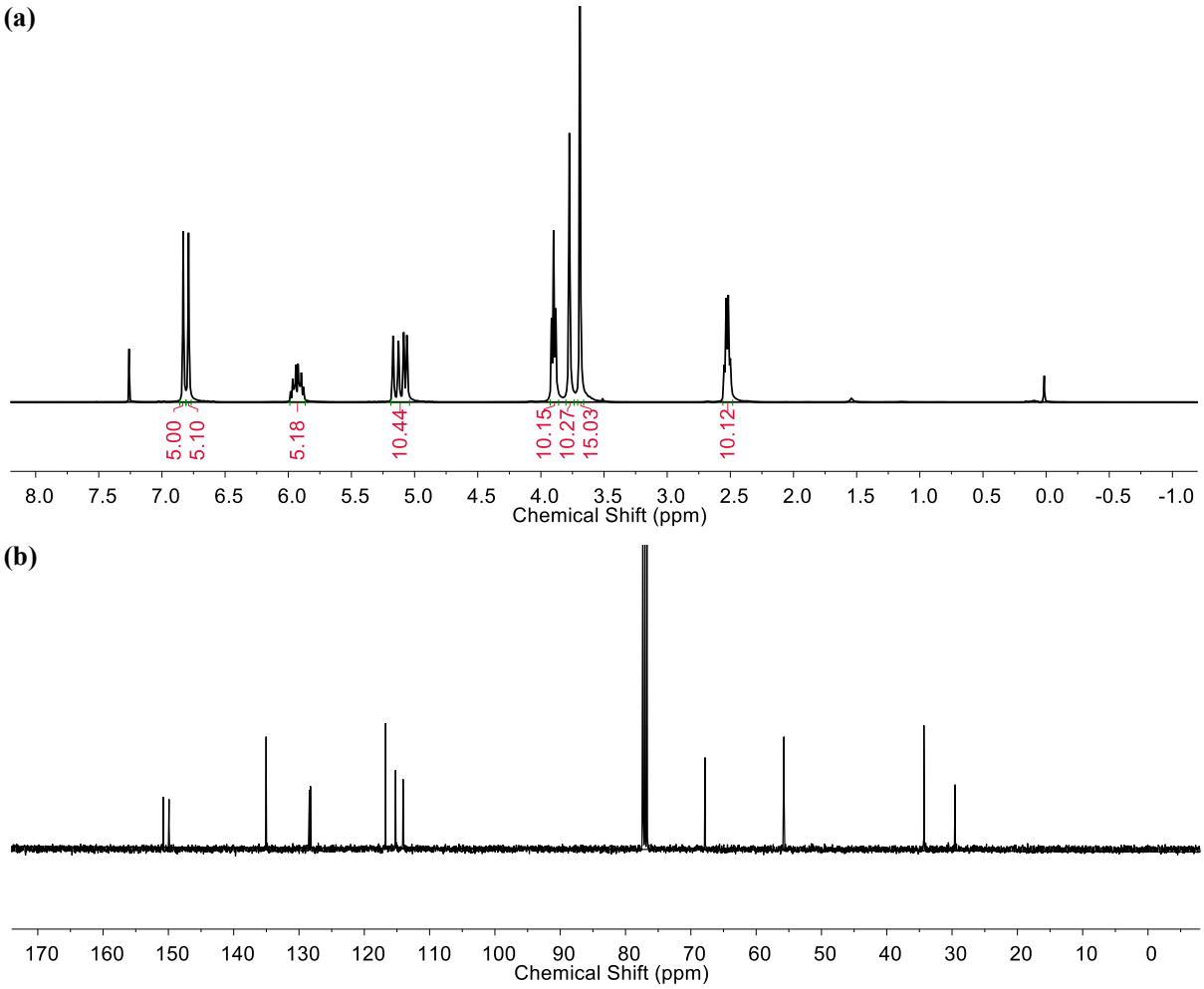
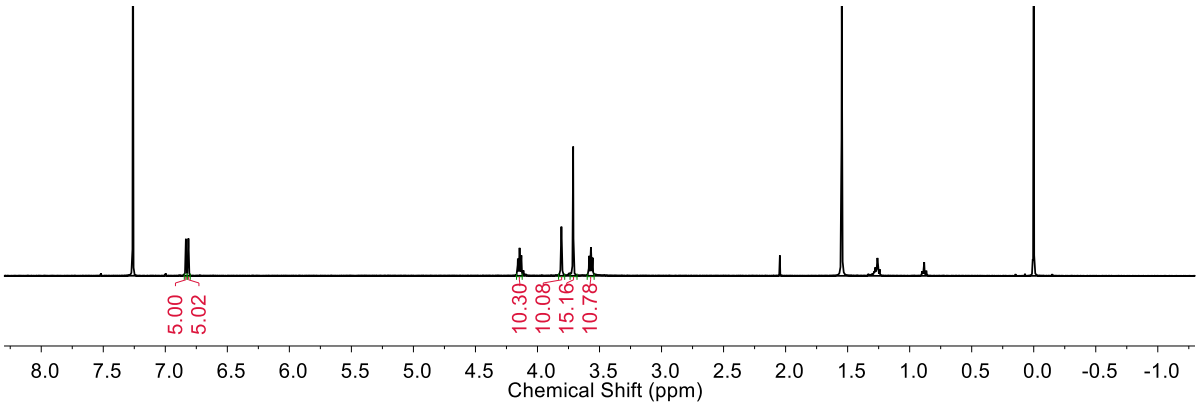


Figure S9. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of (homoallyl)$_5$-tiara-pillar[5]arene **2c** recorded in $CDCl_3$ at 298 K.

(2-Bromoethyl)$_5$-tiara-pillar[5]arene **2d**: To a stirred suspension of **1d** (238 mg, 0.91 mmol) in 1,2-dichloroethane (12 mL) was added $FeCl_3$ (15 mg, 0.09 mmol). The mixture was stirred at 25 °C for 8 h before MeOH (2 mL) was added to quench the reaction. The solvent was removed under reduced pressure to yield a crude product, which was purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (from 1:15 to 1:10) to provide the desired product **2d** as a light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 (s, 5H), 6.74 (s, 5H), 4.09–4.06 (m, 5H), 3.74 (s, 10H), 3.64 (m, 15H), 3.51–3.48 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.4, 149.0, 129.0, 128.5, 116.0, 113.9, 69.1, 55.7, 30.7, 29.7. HRMS (ESI): calcd for $C_{50}H_{55}Br_5O_{10}Na$ $[M + Na]^+$ m/z = 1236.9569, found m/z = 1236.9596.

(a)



(b)

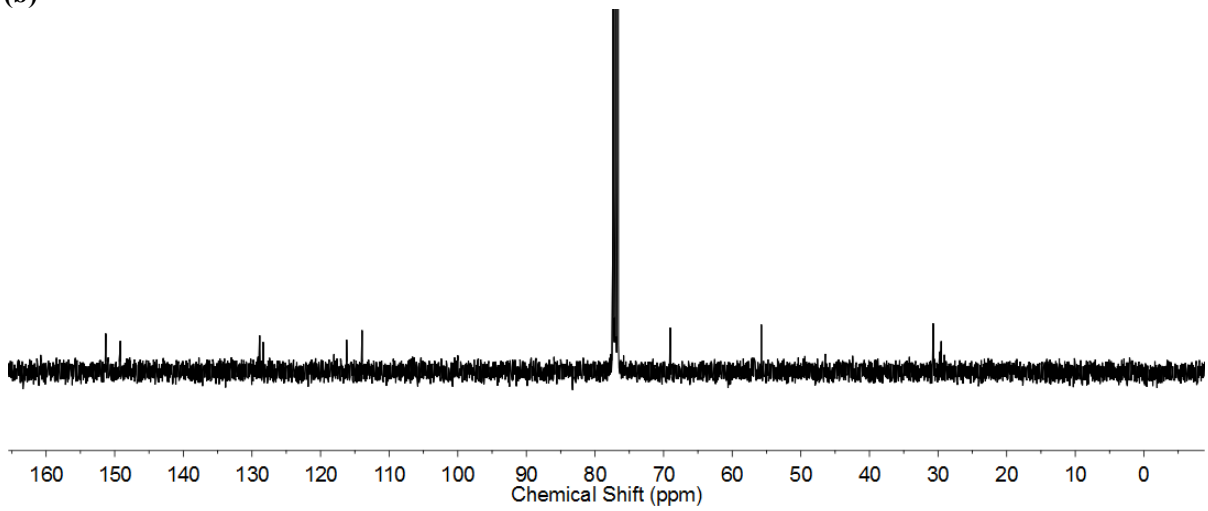


Figure S10. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of (2-bromoethyl)$_5$-tiara-pillar[5]arene **2d** recorded in $CDCl_3$ at 298 K.

(3-Bromopropyl)$_5$-tiara-pillar[5]arene **2e**: To a stirred suspension of **1e** (234 mg, 0.91 mmol) in 1,2-dichloroethane (12 mL) was added $FeCl_3$ (15 mg, 0.09 mmol). The mixture was stirred at 25 °C for 8 h before MeOH (3 mL) was added to quench the reaction. The solvent was removed under reduced pressure to yield a crude product, which was purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (from 1:15 to 1:10) to obtain the product **2e** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 (s, 5H), 6.68 (s, 5H), 3.94 (t, J = 5.6 Hz, 10H), 3.77 (s, 10H), 3.68 (s, 15H), 3.52 (t, J = 6.4 Hz, 10H), 2.20 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1, 149.7, 128.6, 128.3, 115.2, 114.3, 66.3, 56.0, 32.9, 30.6, 29.9. HRMS (ESI): calcd for $C_{55}H_{65}O_{10}Br_5Na$ $[M + Na]^+$ m/z = 1307.0351, found m/z = 1307.0362.

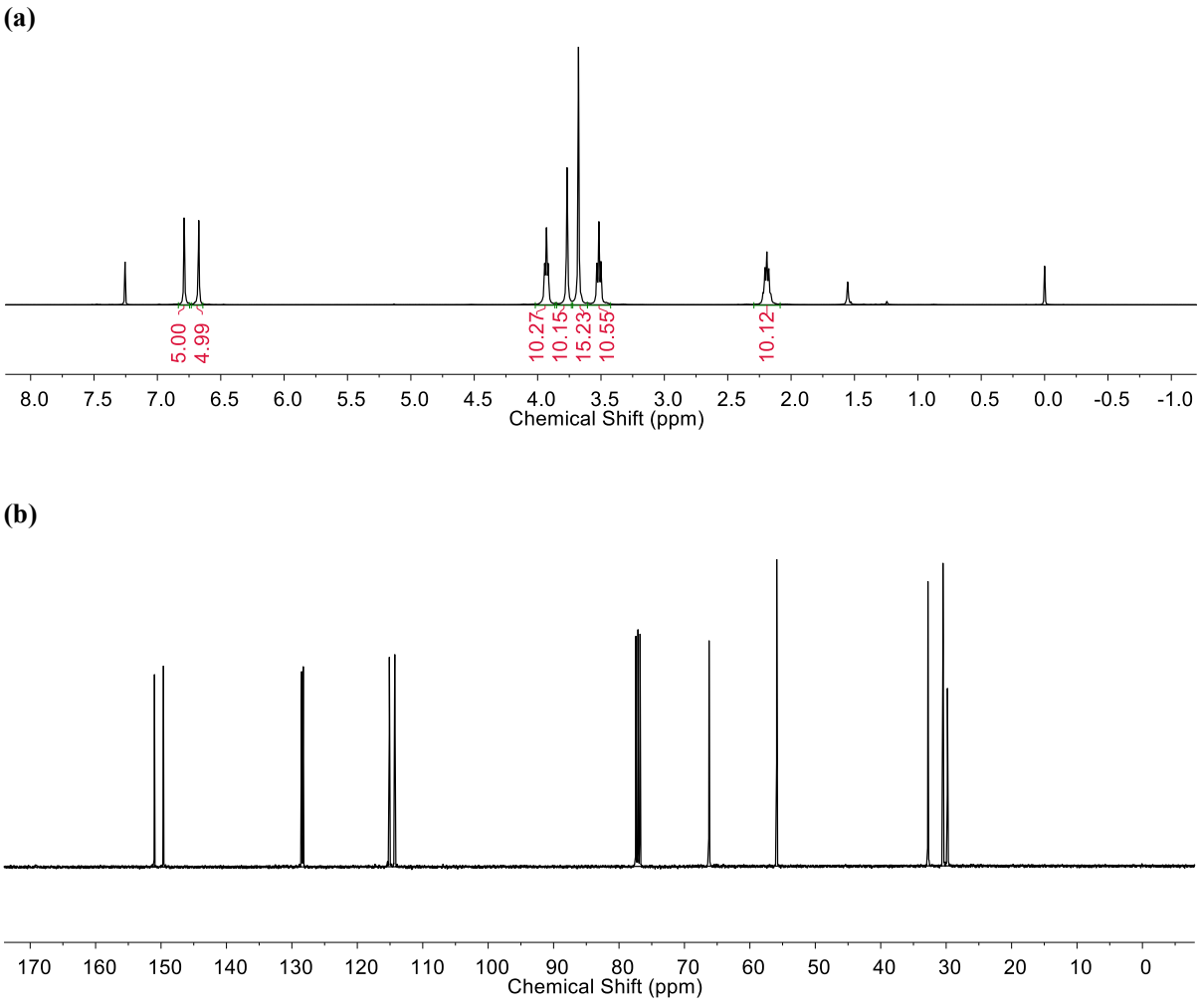
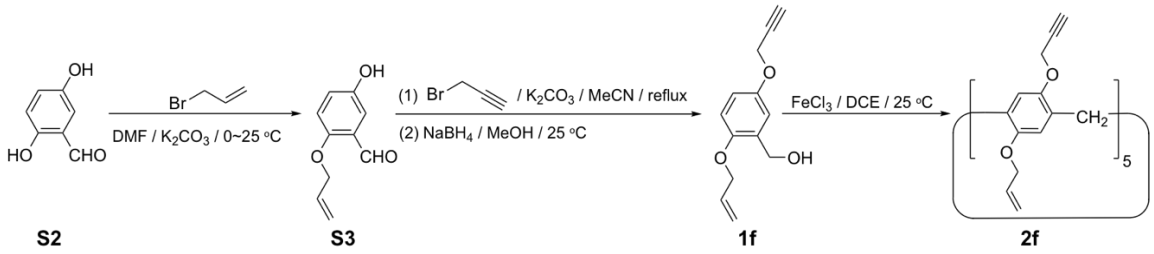


Figure S11. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of (3-bromopropyl)$_5$-tiara-pillar[5]arene **2e** recorded in $CDCl_3$ at 298 K.



Scheme S2. The synthetic route of (propargyl)$_5$(allyl)$_5$-tiara-pillar[5]arene **2f**.

S3: To a mixture of **S2** (1.0 g, 7.25 mmol) and K_2CO_3 (2.07 g, 15 mmol) slurry in DMF (25 mL) was added 3-bromoprop-1-ene (0.96 g, 8.0 mmol). The mixture was stirred in ice bath for 1 h, then stirred at 25 °C for 12 h. The mixture was filtrated and the solvent was then removed under reduced pressure. The crude product was purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (from 1:8 to 1:6) to obtain the product **S3** as a colorless oil (0.52 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.46 (s, 1H), 7.37 (d, J = 3.2 Hz, 1H), 7.10 (m, 1H), 6.91 (d, J = 8.8 Hz, 1H), 6.11–6.01 (m, 1H), 5.45–5.31 (m, 2H), 4.62–4.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.1, 155.7, 150.0, 132.6, 125.5, 123.6, 118.1, 115.0, 113.5, 70.0. HRMS (ESI): calcd for $C_{10}H_{10}O_3Na$ $[M + Na]^+$ m/z = 201.0528, found m/z = 201.0522.

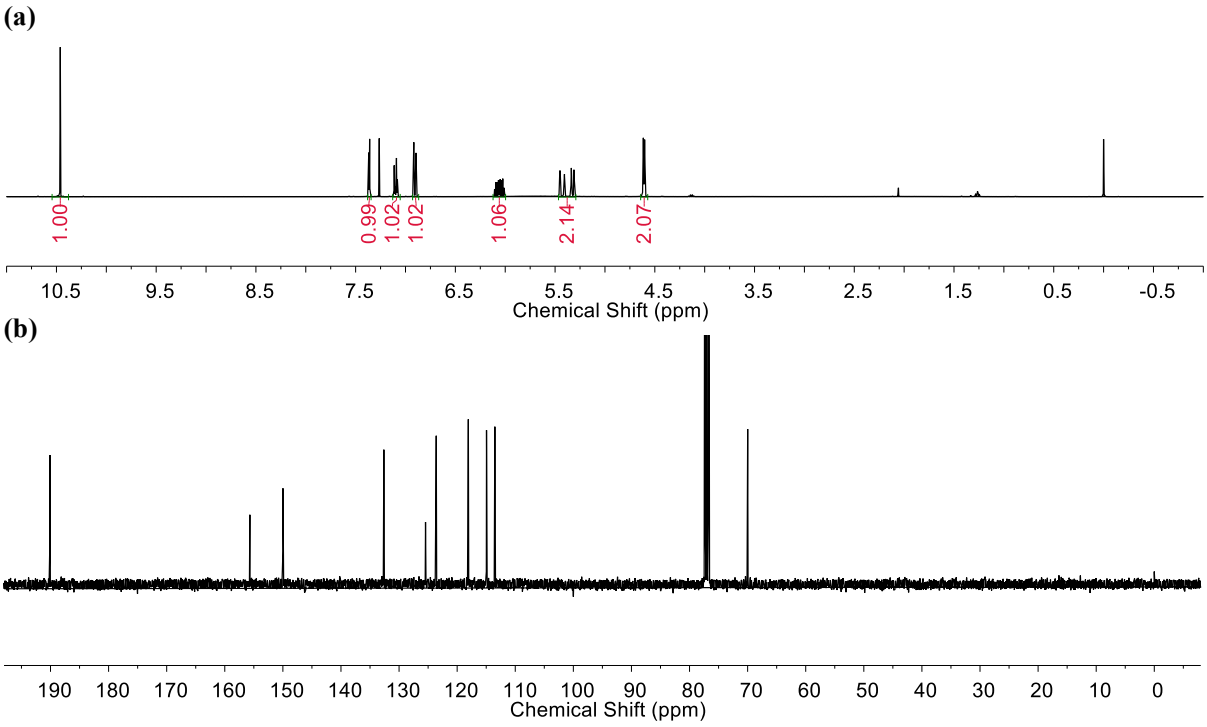


Figure S12. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of **S3** recorded in $CDCl_3$ at 298 K.

1f: To a slurry of **S3** (520 mg, 0.29 mmol) and K_2CO_3 (550 mg, 4 mmol) in MeCN (20 mL) was added 3-bromoprop-1-yne (470 mg, 4.0 mmol). The mixture was sealed and refluxed for 15 h. The reaction mixture was filtered to remove K_2CO_3 and then concentrated. The resulting residue was dissolved in MeOH (20 mL), to which $NaBH_4$ (5.7 mg, 0.15 mmol) was added. The solution was stirred at room temperature for 5 min until TLC indicated the complete conversion from aldehyde to alcohol, and the solvent was then removed under reduced pressure. The crude product was purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (from 1:8 to 1:6) to obtain the product **1f** as a yellow oil (450 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98–6.97 (d, J = 3.2 Hz, 1H), 6.88–6.80 (m, 2H), 6.10–6.00 (m, 1H), 5.42–5.27 (m, 2H), 4.69 (s, 2H), 4.65 (d, J = 2.4 Hz, 2H), 4.56–4.54 (m, 2H), 2.50 (t, J = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.7, 151.2, 133.2, 130.6, 117.6, 116.0, 114.5, 112.5, 78.8, 75.4, 69.4, 62.0, 55.6. HRMS (ESI): calcd for $C_{13}H_{14}O_3Na$ $[M + Na]^+$ m/z = 241.0841, found m/z = 241.0835.

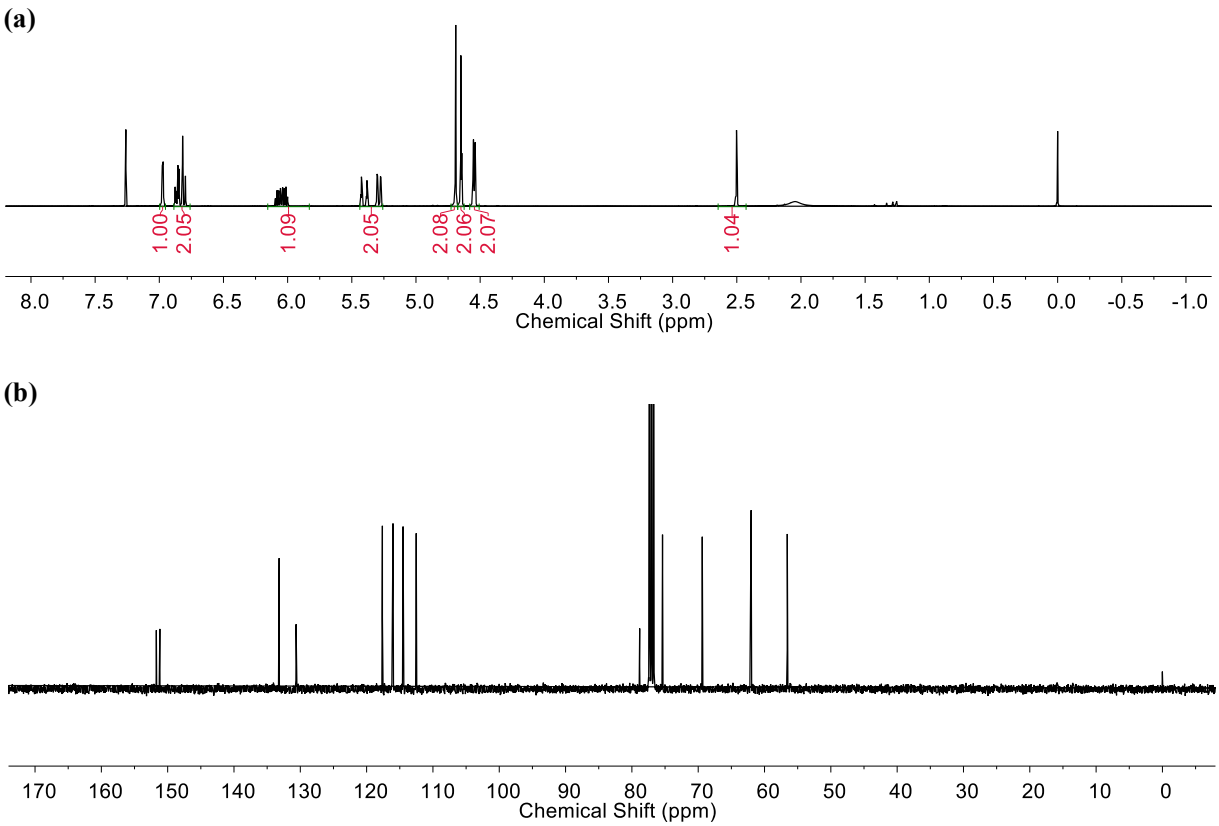
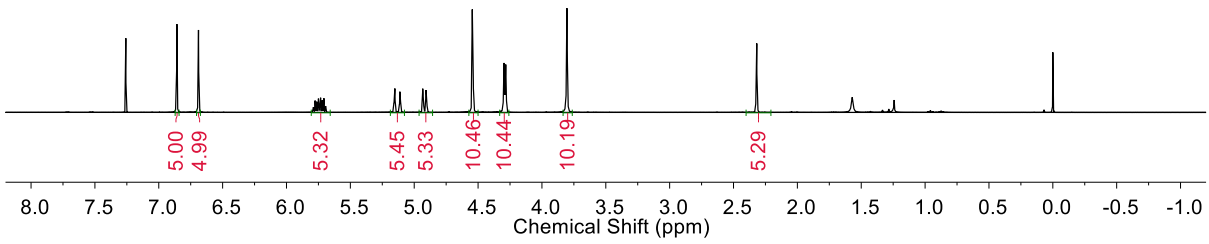


Figure S13. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of **1f** recorded in $CDCl_3$ at 298 K.

(Propargyl)$_5$(allyl)$_5$-tiara-pillar[5]arene **2f**: To a stirred suspension of **1f** (463 mg, 2.00 mmol) in 1,2-dichloroethane (10 mL) was added $FeCl_3$ (33 mg, 0.20 mmol). The mixture was stirred at 25 °C for 8 h before MeOH (2 mL) was added to quench the reaction. The solvent was removed under reduced pressure to yield a crude product, which was purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (from 1:15 to 1:10) to obtain the product **2f** as a light yellow solid (32 mg, 8%). R_f = 0.4 (EtOAc/*n*-hexane= 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 5H), 6.69 (s, 5H), 5.79–5.69 (m, 5H), 5.16–5.10 (m, 5H), 4.93–4.90 (m, 5H), 4.55–4.54 (d, J = 2.4 Hz, 10H), 4.30–4.28 (m, 10H), 3.80 (s, 10H), 2.32–2.31 (t, J = 2.4 Hz, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.1, 148.8, 133.7, 129.0, 128.5, 117.1, 115.7, 115.2, 79.5, 74.8, 69.1, 56.7, 29.8. HRMS (ESI): calcd for $C_{65}H_{60}O_{10}Na$ $[M + Na]^+$ m/z = 1023.4084, found m/z = 1024.4080.

(a)



(b)

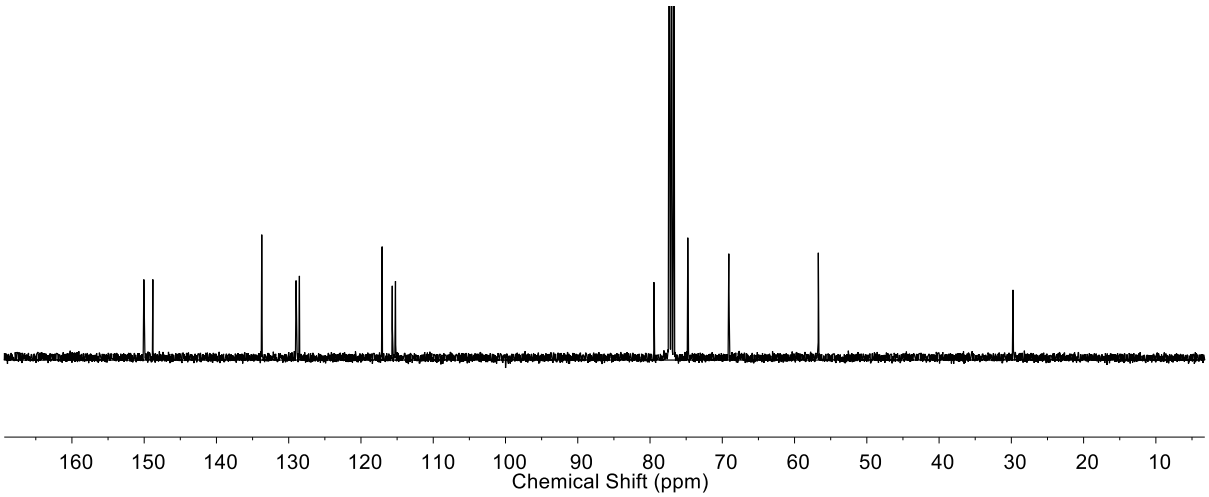
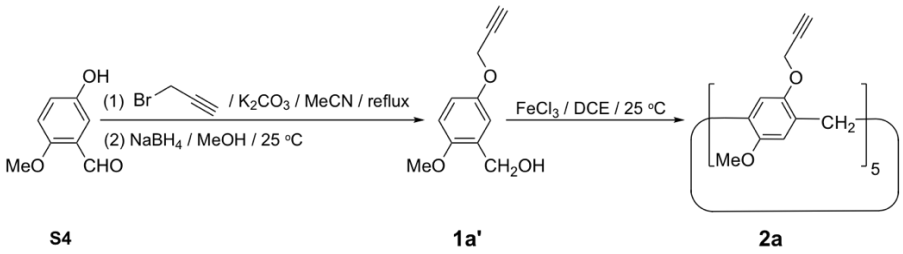


Figure S14. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of (propargyl)$_5$(allyl)$_5$-tiara-pillar[5]arene **2f** recorded in $CDCl_3$ at 298 K.



Scheme S3. Alternative synthetic route to (propargyl)$_5$-tiara-pillar[5]arene **2a**.

1a': To a mixture of **S4**[S2] (2.30 g, 15 mmol) and K_2CO_3 (4.14 g, 30 mmol) slurry in MeCN (40 mL) was added 3-bromoprop-1-yne (3.56 g, 30 mmol). The reaction mixture was sealed and refluxed for 12 h. The reaction mixture was filtered to remove K_2CO_3 and then concentrated. The resulting residue was dissolved in MeOH (30 mL), to which $NaBH_4$ (285 mg, 7.5 mmol) was added. The solution was stirred at room temperature for 10 min, and the solvent was then removed under reduced pressure. The crude product purified by column chromatography on silica-gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (1:10 to 1:3) gradient to provide the product **1a'** as a yellow oil (2.88 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, J = 2.0 Hz, 1H), 6.90-6.88 (m, 1H), 6.82 (d, J = 5.6 Hz, 1H), 4.66 (s, 2H), 4.65 (d, J = 1.6 Hz, 2H), 3.83 (s, 3H), 2.51 (t, J = 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.3, 151.5, 130.2, 116.2, 114.5, 111.0, 78.8, 75.4, 62.1, 55.6, 55.7. HRMS (ESI) calcd for $C_{11}H_{12}O_3Na$ [M + Na^+] m/z = 215.0684; found m/z = 215.0678.

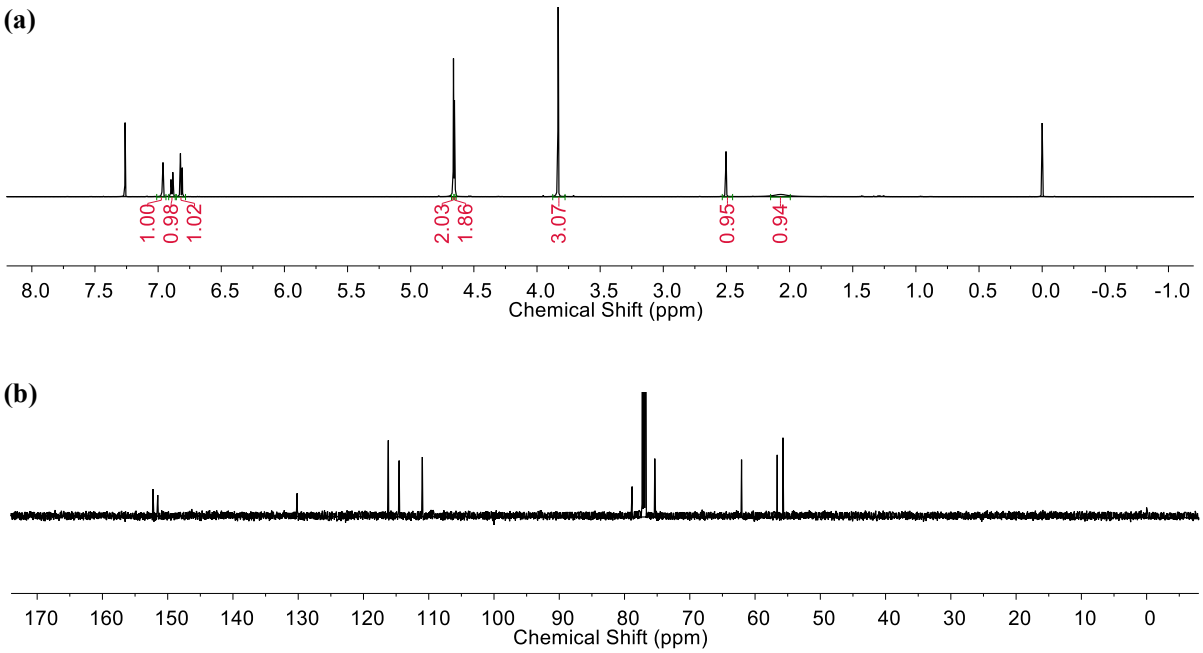
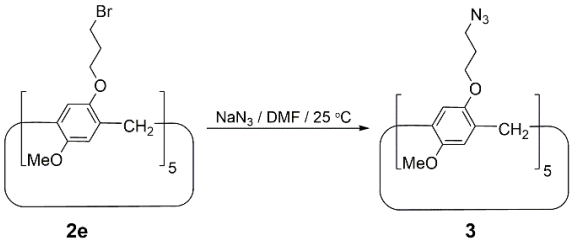


Figure S15. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of **1a'** recorded in $CDCl_3$ at 298 K.

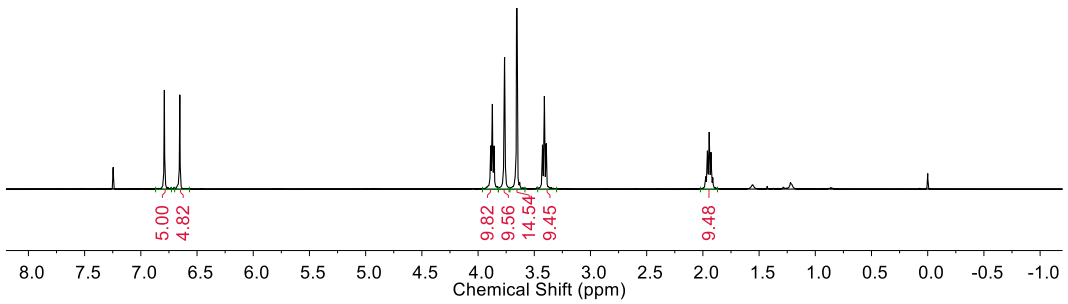


2e **3**

Scheme S4. The synthesis of (3-azidopropyl)$_5$-tiara-pillar[5]arene **3**.

(3-Azidopropyl)$_5$-tiara-pillar[5]arene **3**: To a stirred solution of (3-bromopropyl)$_5$-tiara-pillar[5]arene **2e** (50 mg, 0.039 mmol) in dry DMF (3 mL) was added NaN_3 (15.2 mg, 0.234 mmol). The mixture was stirred at 25 °C for 15 h, after which H_2O was added. The resulting precipitate was extracted with Et_2O (3 × 20 mL), the combined organic layer was washed with H_2O (1 × 30 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography on silica gel (200–300 mesh) using EtOAc/*n*-hexane as eluents (from 1:9 to 1:4) to obtain the product **3** as a white solid (41 mg, 96%). R_f = 0.46 (1:4 EtOAc/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (s, 5H), 6.67 (s, 5H), 3.89 (t, *J* = 6.0 Hz, 10H), 3.78 (s, 10H), 3.67 (s, 15H), 3.42 (t, *J* = 6.8 Hz, 10H), 1.96 (q, *J* = 6.3 Hz, 10H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1, 149.7, 128.6, 128.4, 115.2, 114.4, 65.4, 55.9, 48.5, 29.9, 29.2. HRMS (ESI): calcd for $C_{55}H_{65}O_{10}N_{15}Na$ $[M + Na]^+$ *m*/*z* = 1118.4937, found *m*/*z* = 1118.4939.

(a)



(b)

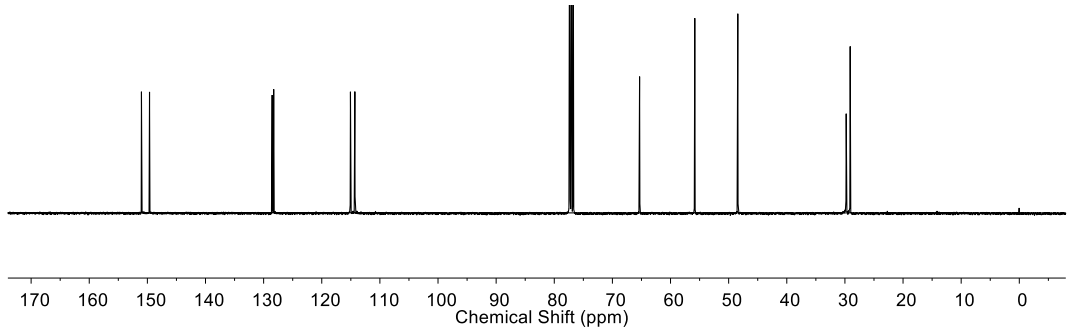


Figure S16. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of (3-azidopropyl)-tiara-pillar[5]arene **3** recorded in $CDCl_3$ at 298 K.

S3. HPLC Characterization

High-performance liquid chromatography (HPLC) analyses were operated using an Agilent 1260 liquid chromatography system (Agilent Technologies, USA), equipped with Agilent 6420 Triple Quad MS system (Agilent Technologies, USA). The separation was performed on an Agilent ZORBAX SB-C_{18} column (150 mm × 4.6 mm, 5 μm) (Agilent Technologies, USA) with mobile phase consisting of solvent A (acetonitrile) and solvent B (pure water). HPLC Grade acetonitrile was purchased from Concord Technology, P. R. China, and water was purified by a Milli-Q water purification system (Merck, Germany). Gradient elution: 0–30 min, linear gradient from 75% A to 95% A (v/v); flow rate of the mobile phase: 1.0 mL/min; wavelength of UV-detection: 214 nm; column temperature: 25 °C; sample injection volume: 5 μL.

The isolation of the isomeric mixture of the (propargyl)$_5$-pillar[5]arenes was performed using a LC-6ADsecondary (2 pumps) semi-preparative HPLC system (Shimadzu Technologies, Japan). The isomeric mixture (20 mg) was dissolved in 1 mL of acetonitrile, and then collected in a single injection by the manual operation with a 1 mL syringe and 1 mL sample loop. The separation was performed on an Agilent ZORBAX SB-C_{18} PrepHT column (21.2 × 250 mm) (Agilent Technologies, USA). The flow rate was 6 mL/min. The mixture was carried out using a linear gradient mix from 75% A to 95% A (v/v).

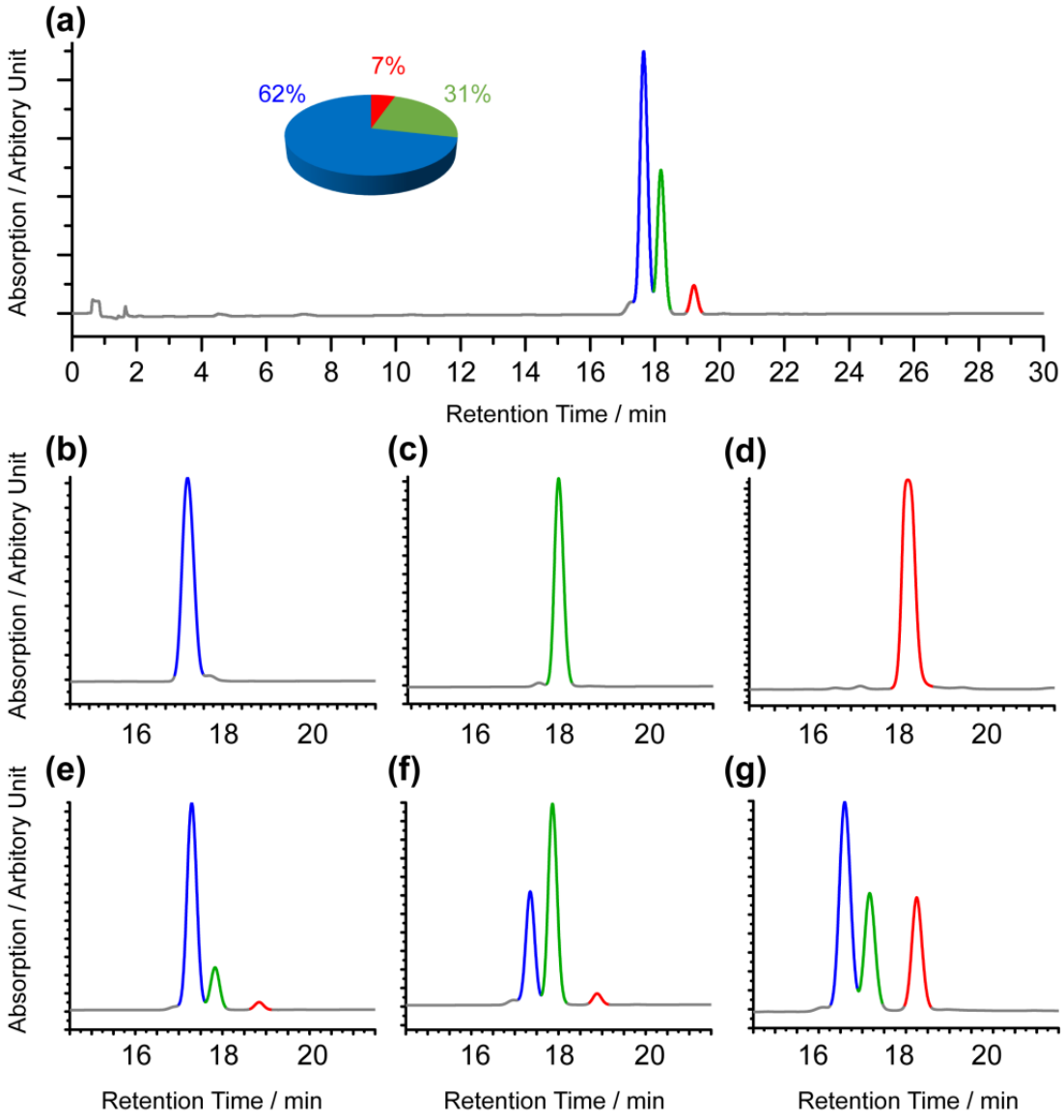


Figure S17. HPLC Analyses and purification of the (propargyl)$_5$-pillar[5]arene isomeric mixture obtained by conventional statistical synthesis protocol. (a) HPLC chromatogram of the isomeric mixture, in which three distinctive peaks in 62:31:7 ratio were observed. The isomeric mixture was subjected to prep-HPLC for purification, and three different fractions corresponding to the three peaks observed in panel a were isolated. HPLC chromatograms of (b-d) the three isolated fractions; (e-g) the three isolated fractions co-injected with the isomeric mixture. From NMR (see Supplementary Information Section S2) and X-ray crystallography (Figure 2 and Supporting Information Section S5) characterizations, it was concluded that the third fraction (labeled in red) is the (propargyl)$_5$-tiara-pillar[5]arene **2a**.

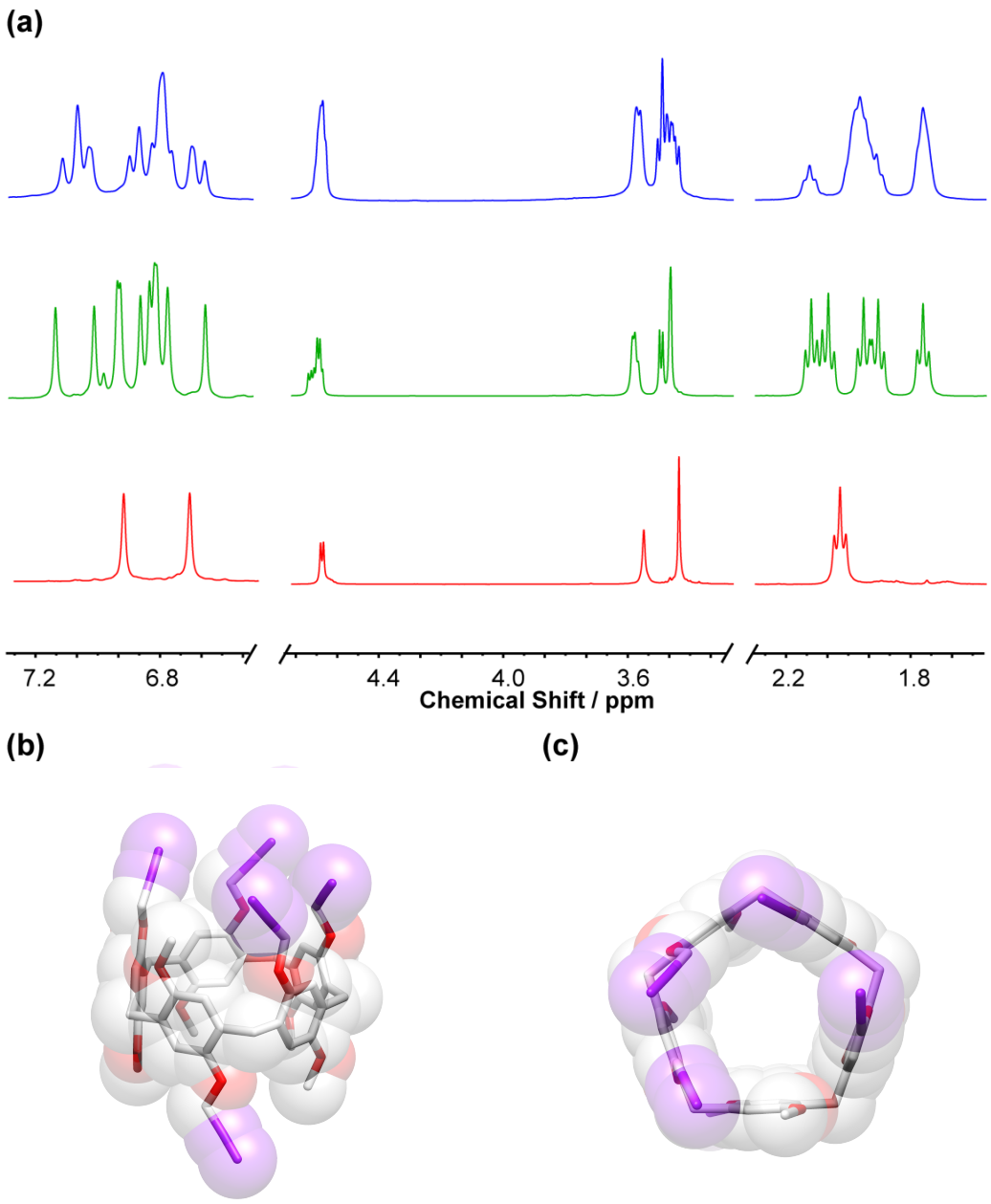


Figure S18. (a) ^{1}H NMR Spectra (400 MHz) of the three fractions isolated by prep-HPLC shown in Figure S17 recorded in $CDCl_3$ at 298 K. The second fraction (labeled in green) was successfully crystallized by slow vapor diffusion of hexane into EtOAc solution containing the second fraction. From X-ray crystallography characterization (see Supporting Information Section S5), it can be unambiguously identified as the $(propargyl)_5$-(A1/B1/C1/D1/E2)-pillar[5]arene **S5**, which has four propargyl groups on one rim and one propargyl on the other. (b) Side view and (c) top view, illustrated as a blend of tubular stick and space-filling representations. Only one of the enantiomeric co-conformations in the solid-state is shown. Guest molecule and all hydrogens are omitted for the sake of clarity. Color code: alkyne, purple; carbon, gray; oxygen, red.

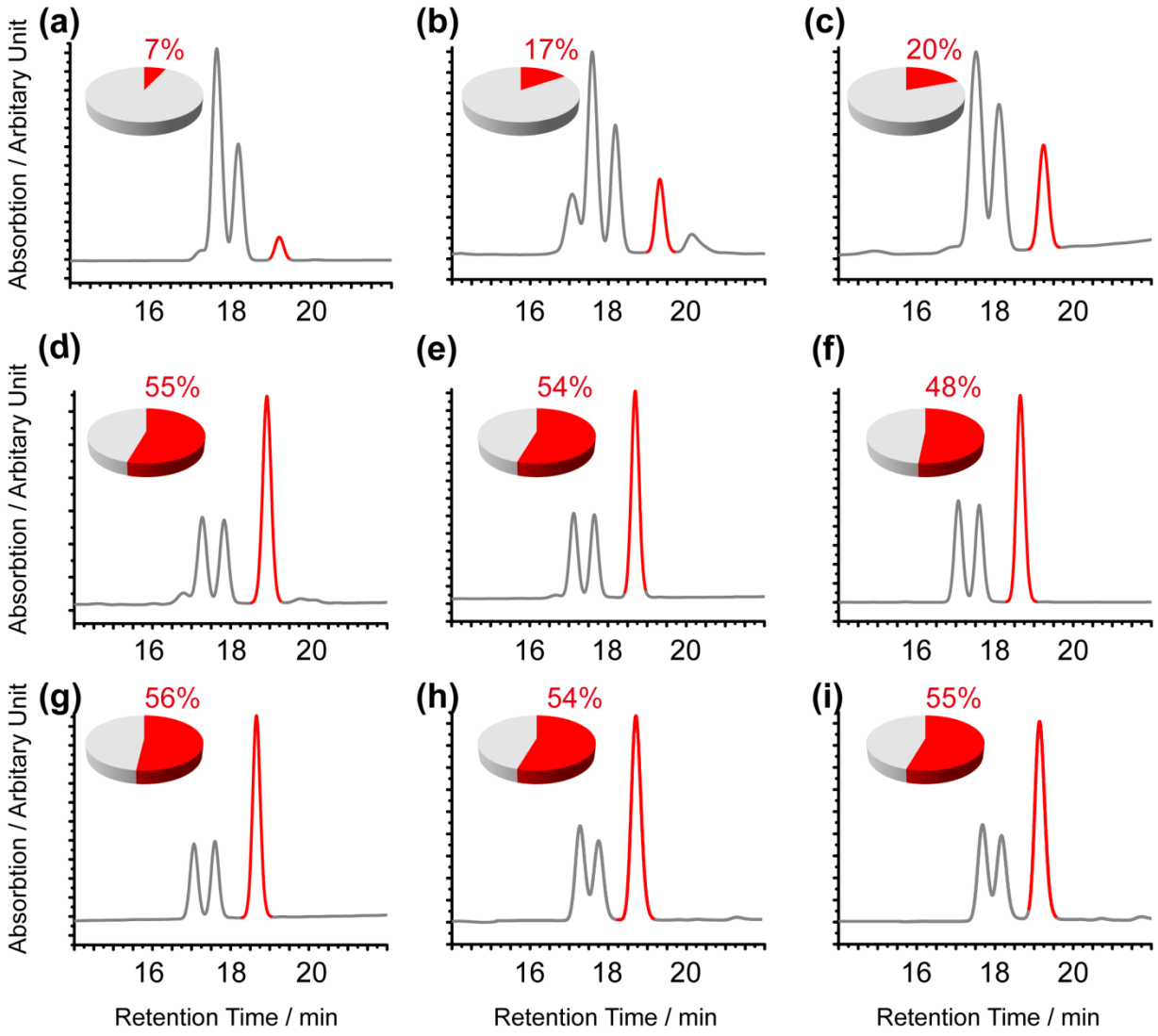
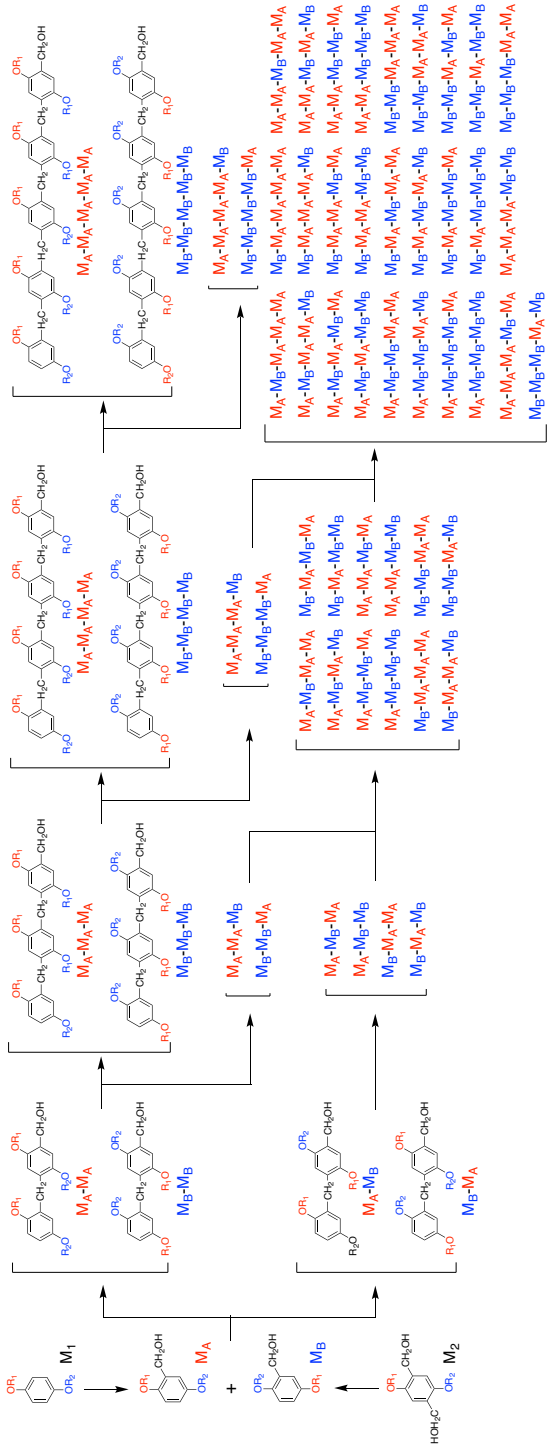


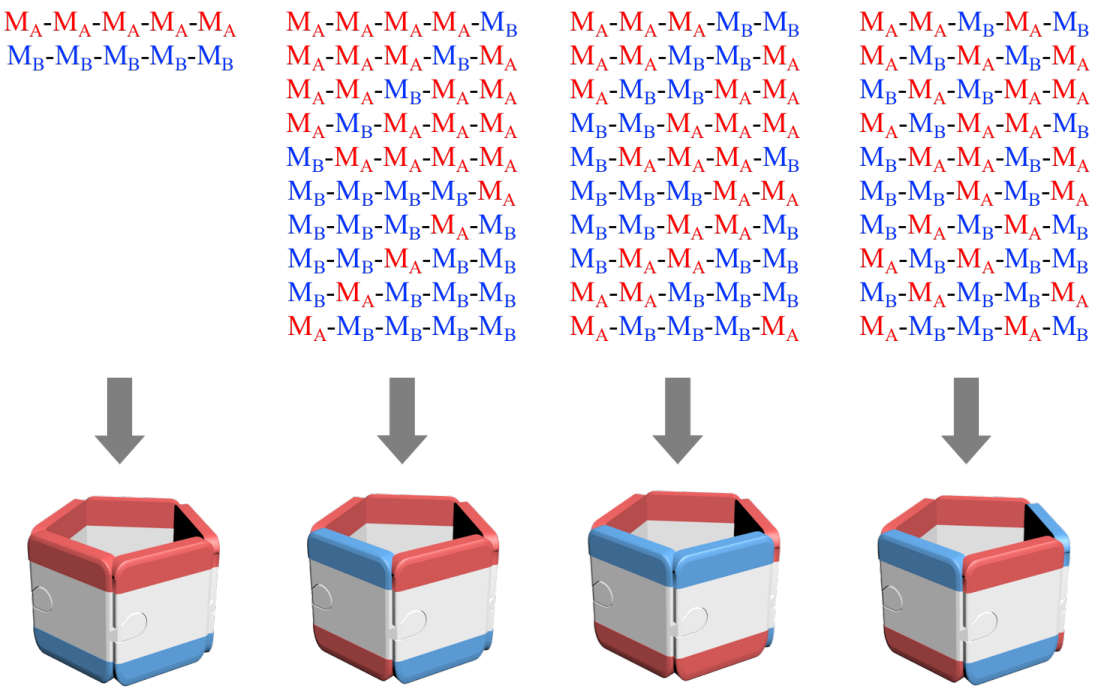
Figure S19. Analytical HPLC chromatograms of reaction mixtures obtained from (a) conventional statistical synthesis protocol, **(b-i)** preoriented strategy with different reaction conditions listed in Table 1: (b) Entry 1; (c) Entry 2; (d) Entry 3; (e) Entry 4; (f) Entry 6; (g) Entry 7; (h) Entry 8; (i) Entry 9. The peaks corresponding to the tiara-pillar[5]arene **2a** are labelled in red. The ratios are calculated based on the integrals of peak areas.

S4. Mechanism and Reaction Pathways Discussions

More detailed reaction pathways of the conventional statistical synthesis (Figure 1a) of tiara-pillar[5]arene (T-P[5]) are depicted in Schemes S5 and S6.



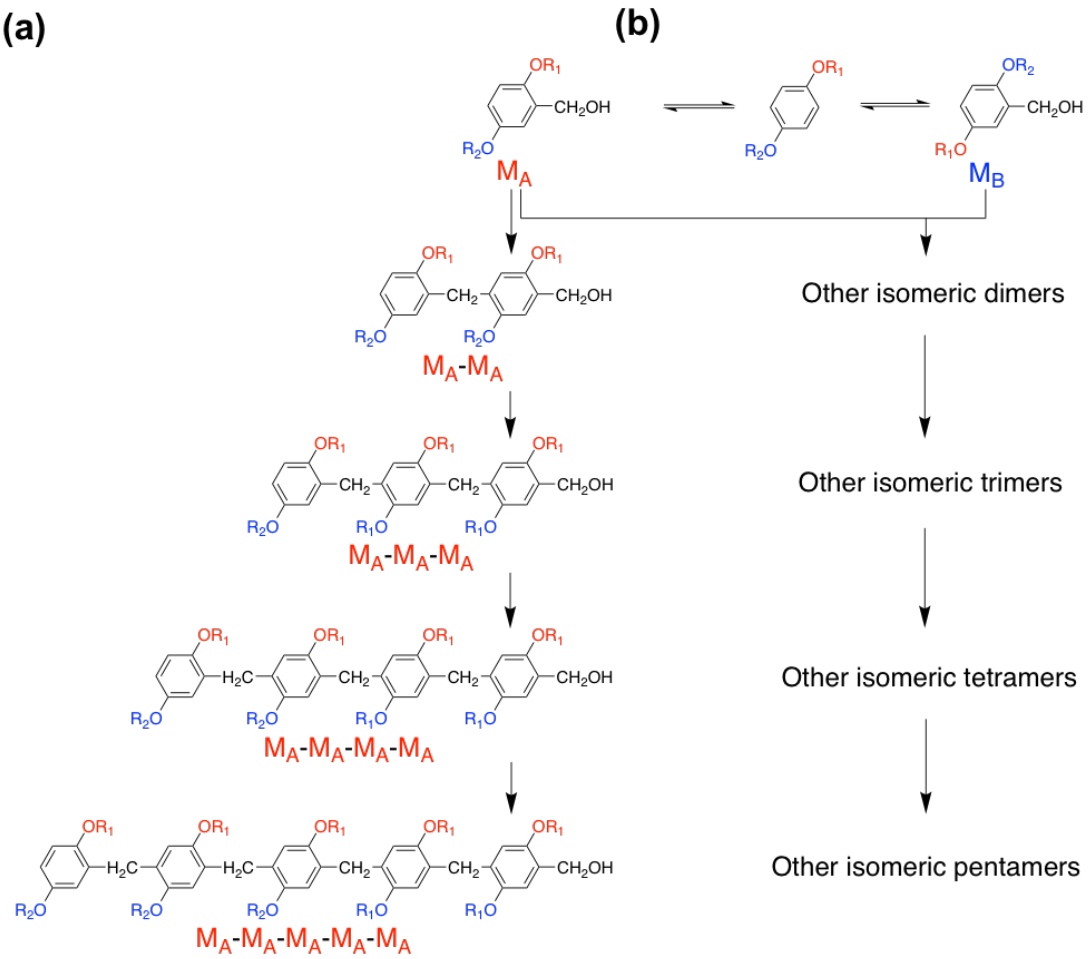
Scheme S5. More detailed reaction pathways for the conventional statistical synthesis of "rim-differentiated" pillar[5]arenes. When 1,4-dialkoxybenzene (**M$_1$**) or 1,4-dialkoxy-2,5-bis(ethoxymethyl)benzene (**M$_2$**) is used as the starting material, two key monomeric intermediates **M$_A$** and **M$_B$** can be generated through Friedel-Crafts alkylation/dealkylation in the presence of a Lewis acid. The dimerization of **M$_A$** and **M$_B$** forms *syn* (**M$_A$**-**M$_A$**, **M$_B$**-**M$_B$**) and *anti* (**M$_A$**-**M$_B$**, **M$_B$**-**M$_A$**) dimers. Further oligomerization steps result in even more complicated mixtures of linear trimers, tetramers and pentamers. Out of the 32 possible linear pentamers, only the all-*syn* pentamers **M$_A$**-**M$_A$**-**M$_A$**-**M$_A$**-**M$_A$** and **M$_B$**-**M$_B$**-**M$_B$**-**M$_B$**-**M$_B$** can eventually form the "rim-differentiated" tiara-pillar[5]arenes. In this scheme, the reactions pathways involving the oligomerization of **M$_1$** and **M$_2$** and the cleavage/reformation of the linear oligomers are omitted for clarity.



Scheme S6. The 32 isomeric linear pentamers listed in Scheme S5 eventually form four different P[5] constitutional isomers after cyclization in 1:5:5:5 ratio. Therefore, T-P[5] can be obtained in ~1/16th ratio of the total of P[5]s in conventional statistical synthesis.

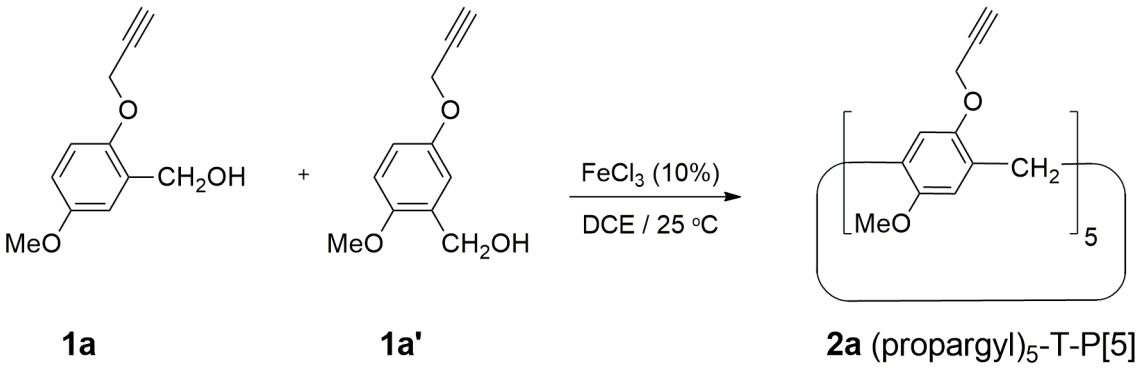
We reasoned that the exclusive use of a starting material identical to one of the intermediates in Figure 1a (or Scheme S5) would minimize the complications during the elongation of linear oligomers. Therefore we proposed the preoriented synthetic protocol (Figure 1c), which employs monomer $\mathbf{M_A}$ equipped with a hydroxymethylene handle at a specific position on the dialkoxylated benzene ring and results in a more selective synthesis of the T-P[5] isomer in the presence of a suitable Lewis acid. A more detailed reaction pathway is depicted in Scheme S7a.

While Figure 1c and Scheme S7a illustrate the ideal situation of exclusive formation of the all-*syn* pentamer and therefore T-P[5], the HPLC analysis in Figure 2c and Figure S19 shows that T-P[5] only accounts for 55% of all the pillar[5]arene macrocycles, revealing that other linear pentamers, which lead to the formations of the non-rim-differentiated P[5] isomer, were also generated during the oligocyclization. This imperfection can be attributed to the cleavage and re-formation of the hydroxymethylene handle through Friedel-Crafts dealkylation/alkylation (see Scheme S7b). In fact, one has to regard the methylene bridge as a dynamic covalent bond under these reaction conditions. These dynamics lead to the formation of non-*syn* linear oligomers and the 45% P[5] isomers that are not T-P[5]. The key difference in the preoriented protocol is that the reaction pathway generating T-P[5] (Scheme S7a) dominates, since the starting materials is exclusively $\mathbf{M_A}$.



Scheme S7. More detailed reaction pathways of the preoriented stragegy for T-P[5]s. (a) The main reaction pathway leading to the all-*syn* linear pentamer and eventually T-P[5], and (b) the side reactions involving the cleavage and re-formation of the hydroxymethylene which lead to the formation of other isomeric oligomers.

Subsequently, we wanted to test our hypothesis that $\mathbf{M_A}$ and $\mathbf{M_B}$ were the key intermediates in the conventional statistical synthesis of rim-differentiated T-P[5]s. Therefore a T-P[5] synthesis was undertaken (Scheme S8) with both compound **1a** (corresponding to $\mathbf{M_A}$) and **1a´** (corresponding to $\mathbf{M_B}$) in 1:1 ratio as the starting materials using the optimized reaction condition (Supporting Information Section S2). The HPLC analysis result shows (Figure S20) that the T-P[5] fraction drops from ~55% to to 6~7%, which is indeed identical to the ratio obtained by the conventional statistical synthesis (Figure 2 and S17).



Scheme S8. Synthesis of (propargyl)$_5$-T-P[5] **2a** from two starting material **1a** and **1a'**.

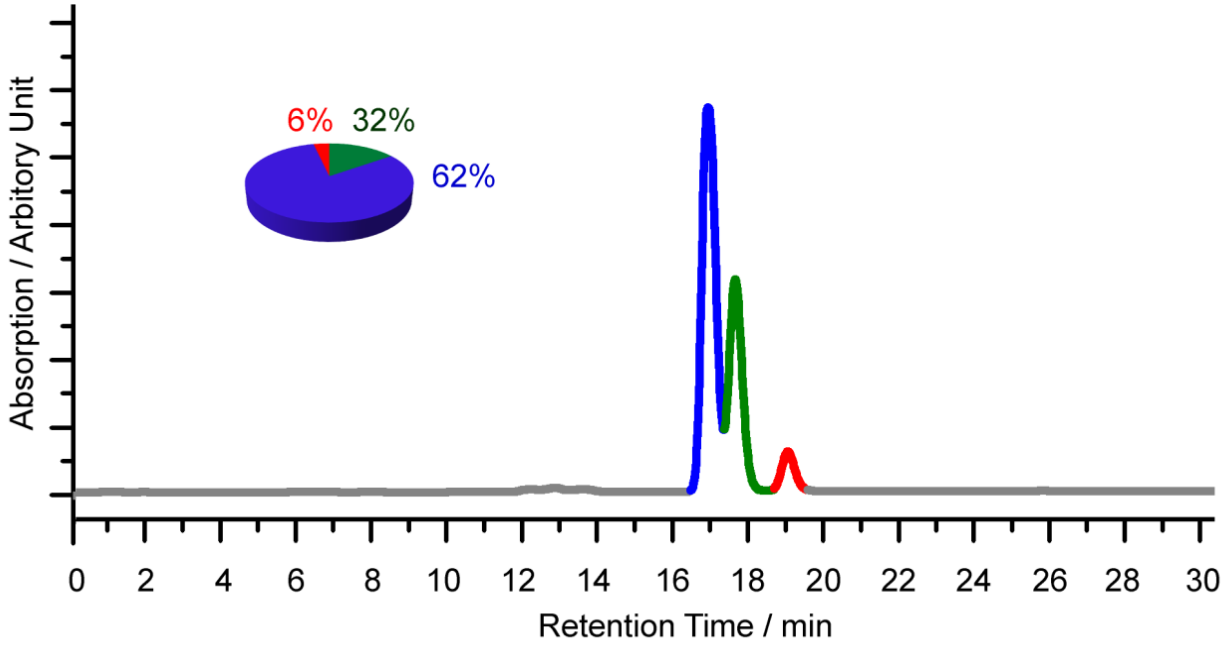


Figure S20. Analytical HPLC chromatograms of reaction mixtures obtained from using equimolar **1a** and **1a'** under the same reaction conditions in the preoriented synthetic protocol.

S5. X-Ray Crystallography

Single crystals of tiara-pillar[5]arene **2a**-**2f** and **3**, and (propargyl)$_5$-(A1/B1/C1/D1/E2)-pillar[5]arene **S5** suitable for X-ray diffraction were selected and mounted in inert oil in cold gas stream and their X-ray diffraction intensity data was collected on a Rigaku MM-007 rotating anode diffractometer equipped with a Rigaku Pilatus 200K hybrid photon counting detector, using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) and Cu *Kα* radiation (λ = 1.54178 Å). Crystals were kept at the temperature listed in Table S1-S8 during data collection. By the use of Olex2,[S3] the structure was solved either (i) with the ShelXT structure solution program using Direct Methods or (ii) with the ShelXM structure solution program using Dual Space and (iii) refined with the ShelXL refinement package using Least Squares minimization.[S4] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Some guest molecules were refined isotropically due to disorder that could not be modeled precisely. Distance restraints were also imposed on some disordered guest hexane molecules. Selected details of the data collection and structural refinement of each compound can be found within the Table S1-S8 and full details are available in the corresponding CIF files. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1559844, 1559785, 1559787, 1559786, 1571589,1571544, 1586557, and 1504990) and may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for (propargyl)$_5$-tiara-pillar[5]arene **2a**.

Empirical formula	$C_{61}H_{64}O_{10}$
Formula weight / g mol^{-1}	957.12
Temperature / K	133
Crystal system	monoclinic
Space group	*C2/c*
a / Å	19.719(2)
b / Å	14.849(2)
c / Å	35.106(3)
α / °	90
β / °	90.104(5)
γ / °	90
Volume / Å^3	10279(2)
Z	8
ρ_{calc} / g cm^{-3}	1.237
μ / mm^{-1}	0.083
F / 000	4080.0
2θ range for data collection / °	6.22 - 55.11
Crystal size / mm^3	0.066 × 0.057 × 0.045
Index ranges	-25 ≤ h ≤ 25, -19 ≤ k ≤ 19, -45 ≤ l ≤ 45
Reflections collected	64336
Independent reflections	11832 [R_{int} = 0.0392, R_{sigma} = 0.0262]
Data / restraints / parameters	11832 / 7 / 877
Goodness-of-fit on F^2	1.035
Final *R* indices [I > 2σ (I)]	R_1 = 0.0620, wR_2 = 0.1502
Final *R* indices [all data]	R_1 = 0.0899, wR_2 = 0.1712
Largest diff. peak / hole / e Å^{-3}	0.65 / -0.44
CCDC No.	1559844

Table S2. Crystal data and structure refinement for $(allyl)_5$-tiara-pillar[5]arene **2b**.

Empirical formula	$C_{61}H_{65}O_{10}$
Formula weight / g mol^{-1}	958.13
Temperature / K	133
Crystal system	triclinic
Space group	*P-1*
a / Å	11.8432(12)
b / Å	12.2389(16)
c / Å	21.236(3)
α / °	81.873(13)
β / °	76.172(12)
γ / °	64.056(10)
Volume / $Å^3$	2685.2(6)
Z	2
ρ_{calc} / g cm^{-3}	1.185
μ / mm^{-1}	0.079
F / 000	1022.0
2θ range for data collection / °	6.084 - 50.018
Crystal size / mm^3	0.2 × 0.2 × 0.2
Index ranges	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-25 \leq l \leq 25$
Reflections collected	28763
Independent reflections	9360 [R_{int}= 0.0627, R_{sigma}= 0.0641]
Data/restraints/parameters	9360/0/703
Goodness-of-fit on F^2	1.018
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0591, wR_2 = 0.1492
Final *R* indices [all data]	R_1 = 0.1060, wR_2 = 0.1734
Largest diff. peak / hole / e $Å^{-3}$	1.14 / -0.35
CCDC No.	1559785

Table S3. Crystal data and structure refinement for (homoallyl)$_5$-tiara-pillar[5]arene **2c**.

Empirical formula	$C_{66}H_{84}O_{10}$
Formula weight / g mol^{-1}	1037.33
Temperature / K	133
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a / Å	12.3445(10)
b / Å	20.6410(15)
c / Å	23.2546(18)
α / °	90
β / °	90
γ / °	90
Volume / Å^3	5925.3(8)
Z	4
ρ_{calc} / g cm^{-3}	1.163
μ / mm^{-1}	0.077
F / 000	2240.0
2θ range for data collection / °	6.176 - 55.294
Crystal size / mm^3	0.2 × 0.2 × 0.2
Index ranges	-16 ≤ h ≤ 16, -26 ≤ k ≤ 26, -29 ≤ l ≤ 29
Reflections collected	76180
Independent reflections	13608 [R_{int} = 0.0513, R_{sigma} = 0.0366]
Data/restraints/parameters	13608/17/784
Goodness-of-fit on F^2	1.021
Final R indices [I > 2σ (I)]	R_1 = 0.0466, wR_2 = 0.1113
Final R indices [all data]	R_1 = 0.0662, wR_2 = 0.1200
Largest diff. peak / hole / e Å^{-3}	0.51 / -0.22
CCDC No.	1559787

Table S4. Crystal data and structure refinement for (2-bromoethyl)$_5$-tiara-pillar[5]arene **2d**.

Empirical formula	$C_{56}H_{63}Br_5O_{10}$
Formula weight / g mol^{-1}	1294.05
Temperature / K	133
Crystal system	triclinic
Space group	*P-1*
a / Å	12.2345(13)
b / Å	14.0997(17)
c / Å	16.955(2)
α / °	86.437(6)
β / °	79.558(6)
γ / °	78.681(6)
Volume / Å^3	2819.4(6)
Z	2
ρ_{calc} / g cm^{-3}	1.524
μ / mm^{-1}	3.605
F / 000	2150.0
2θ range for data collection / °	6.244 - 49.998
Crystal size / mm^3	0.2 × 0.2 × 0.2
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20
Reflections collected	31210
Independent reflections	9855 [R_{int} = 0.0569, R_{sigma} = 0.0586]
Data/restraints/parameters	9855/7/659
Goodness-of-fit on F^2	1.074
Final *R* indices [I > 2σ (I)]	R_1 = 0.0575, wR_2 = 0.1623
Final *R* indices [all data]	R_1 = 0.0845, wR_2 = 0.1745
Largest diff. peak / hole / e Å^{-3}	1.95 / -1.46
CCDC No.	1559786

Table S5. Crystal data and structure refinement for (3-bromopropyl)$_5$-tiara-pillar[5]arene **2e**.

Empirical formula	$C_{60}H_{61}Br_5N_2O_{10}$
Formula weight / g mol^{-1}	1346.86
Temperature / K	133
Crystal system	triclinic
Space group	*P-1*
a / Å	11.9944(10)
b / Å	12.9310(13)
c / Å	21.517(2)
α / °	87.544(8)
β / °	76.492(6)
γ / °	71.424(6)
Volume / Å^3	3074.1(5)
Z	2
ρ_{calc} / g cm^{-3}	1.455
μ / mm^{-1}	3.227
F / 000	2357.0
2θ range for data collection / °	6.14 - 50.00
Crystal size / mm^3	0.2 × 0.2 × 0.2
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -25 ≤ l ≤ 25
Reflections collected	33980
Independent reflections	10744 [R_{int} = 0.0562, R_{sigma}= 0.0614]
Data/restraints/parameters	10744/3/674
Goodness-of-fit on F^2	1.124
Final *R* indices [I > 2σ (I)]	R_1 = 0.0698, wR_2 = 0.2190
Final *R* indices [all data]	R_1 = 0.0928, wR_2 = 0.2293
Largest diff. peak / hole / e Å^{-3}	1.96 / -1.62
CCDC No.	1571589

Table S6. Crystal data and structure refinement for (propargyl)$_5$(allyl)$_5$-tiara-pillar[5]arene **2f**.

Empirical formula	$C_{70.68}H_{59}O_{10}$
Formula weight / g mol^{-1}	1068.36
Temperature / K	133
Crystal system	triclinic
Space group	*P-1*
a / Å	12.0426(17)
b / Å	13.8291(17)
c / Å	19.62(2)
α / °	78.720(8)
β / °	83.606(9)
γ / °	19.662(2)
Volume / Å^3	3138.7(7)
Z	2
ρ_{calc} / g cm^{-3}	1.130
μ / mm^{-1}	0.075
F / 000	1126.0
2θ range for data collection / °	6.1-55.26
Crystal size / mm^3	0.2 × 0.2 × 0.2
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -25 ≤ l ≤ 25
Reflections collected	40274
Independent reflections	14215 [R_{int} = 0.0399, R_{sigma} = 0.0449]
Data/restraints/parameters	14215/9/712
Goodness-of-fit on F^2	1.149
Final *R* indices [I > 2σ (I)]	R_1 = 0.0923, wR_2 = 0.2958
Final *R* indices [all data]	R_1 = 0.1285, wR_2 = 0.3221
Largest diff. peak / hole / e Å^{-3}	1.13 / -0.62
CCDC No.	1571544

Table S7. Crystal data and structure refinement for (3-azidopropyl)$_5$-tiara-pillar[5]arene **3**.

Empirical formula	$C_{55}H_{65}N_{15}O_{10}$
Formula weight / g mol^{-1}	1096.22
Temperature / K	100.01(13)
Crystal system	triclinic
Space group	*P*-1
a / Å	12.6260(3)
b / Å	14.7182(2)
c / Å	17.3130(4)
α / °	77.325(1)
β / °	80.660(1)
γ / °	80.012(1)
Volume / Å^3	3065.4(1)
Z	2
ρ_{calc} / g cm^{-3}	1.188
μ / mm^{-1}	0.693
F / 000	1160.0
2θ range for data collection / °	7.168-149.538
Crystal size / mm^3	0.2 × 0.2 × 0.2
Index ranges	-14 ≤ h ≤ 15, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21
Reflections collected	114440
Independent reflections	12179 [R_{int}= 0.0851, R_{sigma}= 0.0395]
Data/restraints/parameters	12179/0/726
Goodness-of-fit on F^2	1.095
Final *R* indices [I > 2σ (I)]	R_1 = 0.0839, wR_2 = 0.2473
Final *R* indices [all data]	R_1 = 0.0947, wR_2 = 0.2574
Largest diff. peak / hole / e Å^{-3}	1.45/-0.62
CCDC No.	1586557

Table S8. Crystal data and structure refinement for (propargyl)$_5$-(A1/B1/C1/D1/E2)-pillar[5]arene **S5**.

Empirical formula	$C_{61}H_{70}O_{10}$
Formula weight / g mol^{-1}	943.1
Temperature / K	133
Crystal system	monoclinic
Space group	$P2_1/n$
a / Å	18.9755(18)
b / Å	12.7943(12)
c / Å	21.464(2)
α / °	90.00
β / °	98.717(2)
γ / °	90.00
Volume / Å^3	5150.9(9)
Z	4
ρ_{calc} / g cm^{-3}	1.242
μ / mm^{-1}	0.083
F / 000	2064.0
2θ range for data collection / °	6.22 to 50.04
Crystal size / mm^3	0.2 × 0.18 × 0.12
Index ranges	$-21 \le h \le 22$, $-15 \le k \le 15$, $-25 \le l \le 23$
Reflections collected	44142
Independent reflections	9076 [R_{int} = 0.0368, R_{sigma} = 0.0247]
Data/restraints/parameters	9076/240/700
Goodness-of-fit on F^2	1.037
Final *R* indices [I > 2σ (I)]	R_1= 0.0684, wR_2= 0.1906
Final *R* indices [all data]	R_1= 0.0848, wR_2= 0.2039
Largest diff. peak / hole / e Å^{-3}	0.46/-0.41
CCDC No.	1504990

S6. References

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