Intramolecular Triple Heck Reaction.

An Efficient Entry to Fused Tetracycles with a Benzene Core

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Supporting information

Experimental Section

General Techniques. Unless otherwise stated, all reactions were performed under an atmosphere of argon using oven-dried glassware. Solvents were treated prior to use according to the standard methods. All melting points were uncorrected. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were performed using CDCl_3 as the solvent. The commercially available reagents were used as received without further purification. **3**,¹ **4**,² **14**,³ **17**,⁴ (S)-3-buten-2-ol,⁵ $\text{Pd}(\text{PPh}_3)_4$,⁶ $\text{Pd}_2(\text{dba})_3\text{-CHCl}_3$,⁷ were prepared by using the literature procedures.

(1) Preparation of 1,3,5-Tribromo-2,4,6-tri(bromomethyl)benzene 2.⁸ A solution of 1,3,5-tribromo-2,4,6-trimethylbenzene **3** (10.7 g, 30 mmol), NBS (19.20 g, 108 mmol) and benzoyl peroxide (BPO) (0.73 g, 3 mmol) in CCl_4 (150 mL) was refluxed for 4 h. The reaction mixture was filtered immediately when hot and the residual was washed with CCl_4 . The filtrate was cooled to room temperature and the solid appeared. After

filtration, the filtrate was concentrated and the residue was recrystallized from CCl_4 to give **2** (11.46 g, 64%) as a yellow solid, which was used for further transformation. ^1H NMR (300 MHz, CDCl_3) δ 4.92 (s, 6H).

(2) 1,3,5-Tribromo-2,4,6-tris(2',2'-bis(methoxycarbonyl)pent-4'-enyl)benzene (5).

Typical procedure. Procedure A. To a suspension of NaH (0.52 g, 80% in paraffin oil, 17.33 mmol) in THF (30 mL) was added methyl 2-(2'-propenyl)malonate **4** (2.46 g, 14.30 mmol) in THF (10 mL) slowly through a dropping funnel. After the addition, the mixture was stirred for additional 30 min at room temperature. Then, **2** (1.70 g, 2.86 mmol) in THF (10 mL) was added dropwise at room temperature. After the mixture was stirred at room temperature for 19.5 h, the reaction was quenched with water, extracted with ether, and washed with brine. The combined organic extracts were dried over MgSO_4 and evaporated. The crude product was further purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **5** (1.28 g, 52%) as a white solid; mp: 78-79°C (ethyl acetate-hexane); ^1H NMR (300 MHz, CDCl_3) δ 5.95-5.70 (m, 3H), 5.15-4.95 (m, 6H), 4.01 (s, 6H), 3.63 (s, 18H), 2.64 (d, J = 6.86 Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 171.0, 138.1, 133.5, 130.3, 118.5, 57.8, 52.4, 43.0, 39.8; IR (KBr) ν = 2951, 1728, 1452, 1433, 1322, 1256, 1224, 1208, 1090, 845 cm^{-1} ; MS (70 eV, EI) m/z (%): 789 ($\text{M}^+ - \text{Br}$ ($2 \times ^{81}\text{Br}$), 55.41), 787 ($\text{M}^+ - \text{Br}$ ($1 \times ^{81}\text{Br}$, $1 \times ^{79}\text{Br}$), 100), 785 ($\text{M}^+ - \text{Br}$ ($2 \times ^{79}\text{Br}$), 50.79); Anal. calcd for $\text{C}_{33}\text{H}_{39}\text{O}_{12}\text{Br}_3$: C, 45.70; H, 4.53. Found: C, 45.86; H, 4.52.

(3) 1,3,5-Tribromo-2,4,6-tri(but-3'-enyl)benzene (7). Typical procedure. Procedure B.

A solution of **2** (3.50 g, 5.89 mmol) in Et_2O (20 mL) was treated with allyl magnesium bromide, which was prepared from magnesium (3.70 g, 154.17 mmol) and allyl bromide

(8.4 g, 69.42 mmol) in Et₂O (50 mL). After being stirred at room temperature for 0.5 h, the reaction was quenched with saturated solution of NH₄Cl (3.70 g, 69.16 mmol), extracted with ether, and washed with brine. The combined organic extracts were dried over MgSO₄ and evaporated. The crude product was further purified by flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 20:1) to give **7** (2.15 g, 78%) as a white solid; mp: 67-68°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 6.10-5.82 (m, 3H), 5.10 (d, *J* = 15.61 Hz, 3H), 5.03 (d, *J* = 10.36 Hz, 3H), 3.35-3.00 (m, 6H), 2.50-2.10 (m, 6H); IR (KBr) ν = 2949, 1642, 1453, 1369, 993cm⁻¹; MS (70 eV, EI) *m/z* (%): 480 (M⁺ (3 × ⁸¹Br), 3.18), 478 (M⁺ (2 × ⁸¹Br, 1 × ⁷⁹Br), 9.75), 476 (M⁺ (1 × ⁸¹Br, 2 × ⁷⁹Br), 10.36), 474 (M⁺ (3 × ⁷⁹Br), 3.44), 28 (100.00); Anal. calcd for C₁₈H₂₁Br₃: C, 45.32; H, 4.44. Found: C, 45.40; H, 4.39.

(4) 1,3,5-Tribromo-2,4,6-tri(allyloxymethyl)benzene (8). Typical procedure. Procedure C. To a suspension of NaH (0.50 g, 80% in paraffin oil, 16.67 mmol) in THF (5 mL) was added allyl alcohol (0.78 g, 13.45 mmol) slowly through a dropping funnel. After the addition, the mixture was stirred for additional 20 min at room temperature. Then, **2** (2.00 g, 3.37 mmol) in THF (10 mL) was added dropwise at room temperature. After the mixture was stirred at room temperature for 16 h, the reaction was quenched with water, extracted with ether, and washed with brine. The combined organic extracts were dried over MgSO₄ and evaporated. The crude product was further purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give **8** (0.88 g, 50%) as a white solid; mp: 54°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 6.07-5.89 (m, 3H), 5.34 (d, *J* = 17.28 Hz, 3H), 5.21 (d, *J* = 10.34 Hz, 3H), 4.92 (s, 6H), 4.11 (d, *J* = 5.59 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 153.8, 132.6, 119.0, 110.8, 74.1; IR (KBr) ν

= 2891, 2842, 1538, 1475, 1360, 1344, 1126, 1080, 1000, 925 cm^{-1} ; MS (70 eV, EI) m/z (%): 359 ($M^+ - 3 \times \text{C}_3\text{H}_4\text{O} - \text{H}$ ($3 \times {}^{81}\text{Br}$), 41.44), 357 ($M^+ - 3 \times \text{C}_3\text{H}_4\text{O} - \text{H}$ ($2 \times {}^{81}\text{Br}$, $1 \times {}^{79}\text{Br}$), 100.00), 355 ($M^+ - 3 \times \text{C}_3\text{H}_4\text{O} - \text{H}$ ($1 \times {}^{81}\text{Br}$, $2 \times {}^{79}\text{Br}$), 98.88), 353 ($M^+ - 3 \times \text{C}_3\text{H}_4\text{O} - \text{H}$ ($3 \times {}^{79}\text{Br}$), 36.82); Anal. calcd for $\text{C}_{18}\text{H}_{21}\text{O}_3\text{Br}_3$: C, 41.17; H, 4.02. Found: C, 41.10; H, 4.07.

(5) 1,3,5-Tribromo-2,4,6-tris((1'-methyl-2'propenyl)methyl)benzene (9). Typical procedure. Procedure D. To a suspension of NaH (0.53 g, 60% in paraffin oil, 13.25 mmol) in THF (5 mL) was added 3-buten-2-ol (0.87 g, 12.13 mmol) in THF (5 mL) slowly through a dropping funnel. After the addition, the mixture was stirred for additional 30 min at room temperature, HMPA (1 mL) was added. After 5 min, **2** (2.00 g, 3.37 mmol) in THF (10 mL) was added dropwise at room temperature. After the mixture was stirred at room temperature for 4.5 h, the reaction was quenched with water, extracted with ether, and washed with brine. The combined organic extracts were dried over MgSO_4 and evaporated. The crude product was further purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give **9** (1.09 g, 57%) as a white solid; mp: 46°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 5.95-5.78 (m, 3H), 5.29 (d, $J = 17.11$ Hz, 3H), 5.18 (d, $J = 10.33$ Hz, 3H), 4.95 (d, $J = 10.12$ Hz, 3H), 4.70 (d, $J = 10.12$ Hz, 3H), 4.10-3.95 (m, 3H), 1.27 (d, $J = 6.42$ Hz, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.0, 137.5, 130.5, 116.0, 76.6, 72.1, 21.3; IR (KBr) $\nu = 2976, 2929, 1541, 1367, 1316, 1084, 992, 924$ cm^{-1} ; MS (70 eV, EI) m/z (%): 358 ($M^+ - 3 \times \text{C}_4\text{H}_6\text{O} + 1$ ($3 \times {}^{81}\text{Br}$), 34.66), 356 ($M^+ - 3 \times \text{C}_4\text{H}_6\text{O} + 1$ ($2 \times {}^{81}\text{Br}$, $1 \times {}^{79}\text{Br}$), 97.75), 354 ($M^+ - 3 \times \text{C}_4\text{H}_6\text{O} + 1$ ($1 \times {}^{81}\text{Br}$, $2 \times {}^{79}\text{Br}$), 100.00), 353 ($M^+ - 3 \times \text{C}_4\text{H}_6\text{O}$ ($3 \times {}^{79}\text{Br}$), 35.19); Anal. calcd for $\text{C}_{21}\text{H}_{27}\text{O}_3\text{Br}_3$: C, 44.47; H, 4.80. Found: C, 44.43; H, 4.83.

(6) 1,3,5-Tribromo-2,4,6-tris(((1S)-methyl-2'propenyl)methyl)benzene (S,S,S)-9.

Following procedure D, (S)-3-buten-2-ol (0.61 g, 8.47 mmol) in THF (5 mL) was treated sequentially with NaH (0.24 g, 95% in paraffin oil, 9.50 mmol, 30 min) in THF (10 mL), HMPA (1 mL) and **2** (1.4 g, 2.36 mmol, 5 h) in THF (5 mL) to give (S,S,S)-**9** (1.00 g, 56%) as a white solid; mp: 53-4°C (petroleum ether); ¹H NMR (300 MHz, CDCl₃) δ 5.95-5.80 (m, 3H), 5.29 (d, *J* = 16.80 Hz, 3H), 5.18 (d, *J* = 10.20 Hz, 3H), 4.95 (d, *J* = 10.50 Hz, 3H), 4.71 (d, *J* = 10.50 Hz, 3 H), 4.08-3.98 (m, 3H), 1.28 (d, *J* = 6.30 Hz, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 139.9, 137.5, 130.5, 116.1, 77.5, 72.1, 21.3; IR (film) ν = 2977, 1540, 1367, 1316, 1134, 991, 925 cm⁻¹; [α]_D²⁰ = +5.0° (c 1.2, chloroform).

(7) 1,3,5-Tribromo-2-(allyloxymethyl)-4,6-bis(bromomethyl)benzene (10) and 1,3,5-tribromo-2,4-bis(allyloxymethyl)-6-(bromomethyl)benzene (11).

Following procedure C, allyl alcohol (1.64 g, 28.28 mmol) in THF (15 mL) was treated sequentially with NaH (0.94 g, 80% in paraffin oil, 31.33 mmol, 20 min) in THF (60 mL) and **2** (8.00 g, 13.47 mmol, 4.5 h) in THF (15 mL) to give **10** (2.25 g, 29%) and **11** (2.23 g, 30%); the data of **10**: white solid: mp 120-121°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 6.10-5.85 (m, 1H), 5.36 (d, *J* = 17.27 Hz, 1H), 5.24 (d, *J* = 10.35 Hz, 1H), 4.93 (s, 4H), 4.90 (s, 2H), 4.13 (d, *J* = 5.00 Hz, 2H); IR (KBr) ν = 3048, 1535, 1425, 1369, 1210, 1085, 978, 860 cm⁻¹; MS (70 eV, EI) *m/z* (%): 439 (M⁺ - Br - 3 × C₃H₄O (4 × ⁸¹Br), 15.66), 437 (M⁺ - Br - 3 × C₃H₄O (3 × ⁸¹Br, 1 × ⁷⁹Br), 65.13), 435 (M⁺ - Br - 3 × C₃H₄O (2 × ⁸¹Br, 2 × ⁷⁹Br), 100.00), 433 (M⁺ - Br - 3 × C₃H₄O (1 × ⁸¹Br, 3 × ⁷⁹Br), 69.71), 331 (M⁺ - Br - 3 × C₃H₄O (4 × ⁷⁹Br), 17.79). The data of **11**: white solid: mp 71-72°C (hexane); ¹H NMR (300 MHz, CDCl₃) δ 6.10-5.85 (m, 2H), 5.34 (d, *J* = 17.08 Hz, 2H), 5.22 (d, *J* = 10.31 Hz, 2H), 4.94 (s, 2H), 4.91 (s, 4H), 4.11 (d, *J* = 5.63 Hz, 4H); IR (KBr) ν = 2850, 1537, 1479, 1428,

1369, 1348, 1214, 1081, 937 cm^{-1} ; MS (70 eV, EI) m/z (%): 359 ($M^+ - \text{Br} - 2 \times \text{C}_3\text{H}_4\text{O}$ ($3 \times {}^{81}\text{Br}$), 28.72), 357 ($M^+ - \text{Br} - 3 \times \text{C}_3\text{H}_4\text{O}$ ($2 \times {}^{81}\text{Br}$, $1 \times {}^{79}\text{Br}$), 90.82), 355 ($M^+ - \text{Br} - 3 \times \text{C}_3\text{H}_4\text{O}$ ($1 \times {}^{81}\text{Br}$, $2 \times {}^{79}\text{Br}$), 100.00), 353 ($M^+ - \text{Br} - 3 \times \text{C}_3\text{H}_4\text{O}$ ($3 \times {}^{79}\text{Br}$), 40.16). Both compounds were used for further transformation without further characterization.

(8) 1,3,5-Tribromo-2-(allyloxymethyl)-4,6-bis(1'-methyl-2'-propenoxymethyl)-benzene (12). Following procedure C, 3-buten-2-ol (0.61 g, 8.40 mmol) in THF (5 mL) was treated sequentially with NaH (0.37 g, 60% in paraffin oil, 9.24 mmol, 20 mmol) in THF (15 mL) and **10** (2.00 g, 3.50 mmol, 3 h) in THF (5 mL) to give **12** (0.91 g, 47%) as a white solid; mp: 35°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 6.08-5.75 (m, 3H), 5.45-5.08 (m, 6H), 5.05-4.80 (m, 4H), 4.70 (d, $J = 10.10$ Hz, 2H), 4.10 (d, $J = 5.51$ Hz, 2H), 4.07-3.90 (m, 2H), 1.27 (d, $J = 6.3$ Hz, 6H); IR (KBr) $\nu = 2976, 1540, 1367, 1133, 1085, 992, 925$ cm^{-1} ; MS (70 eV, EI) m/z (%): 358 ($M^+ + 1 - 2 \times \text{C}_4\text{H}_6\text{O} - \text{C}_3\text{H}_4\text{O}$ ($3 \times {}^{81}\text{Br}$), 35.08), 356 ($M^+ + 1 - 2 \times \text{C}_4\text{H}_6\text{O} - \text{C}_3\text{H}_4\text{O}$ ($2 \times {}^{81}\text{Br}$, $1 \times {}^{79}\text{Br}$), 98.89), 354 ($M^+ + 1 - 2 \times \text{C}_4\text{H}_6\text{O} - \text{C}_3\text{H}_4\text{O}$ ($1 \times {}^{81}\text{Br}$, $2 \times {}^{79}\text{Br}$), 100.00), 352 ($M^+ + 1 - 2 \times \text{C}_4\text{H}_6\text{O} - \text{C}_3\text{H}_4\text{O}$ ($3 \times {}^{79}\text{Br}$), 35.95); Anal. calcd for $\text{C}_{20}\text{H}_{25}\text{O}_3\text{Br}_3$: C, 43.43; H, 4.56. Found: C, 43.46; H, 4.43.

(9) 1,3,5-Tribromo-2-(allyloxymethyl)-4,6-bis((1S)'-methyl-2'-propenoxymethyl)-benzene (S,S)-12. Following procedure C, (S)-3-buten-2-ol (0.36 g, 5.00 mmol) in THF (5 mL) was treated sequentially with NaH (0.13 g, 95% in paraffin oil, 5.15 mmol, 30 min) in THF (10 mL) and **10** (1.20 g, 2.10 mmol, 3.5 h) in THF (5 mL) to give (S,S)-**12** (0.54 g, 46%) as a liquid; ^1H NMR (300 MHz, CDCl_3) δ 6.05-5.80 (m, 3H), 5.40-5.18 (m, 6H), 4.97 (d, $J = 10.20$ Hz, 2H), 4.93 (s, 2H), 4.73 (d, $J = 10.20$ Hz, 2H), 4.11 (dt, $J = 5.4$ and 0.9 Hz, 2H), 4.08-3.96 (m, 2H), 1.29 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 139.9, 137.5, 137.1, 134.5, 130.7, 130.5, 117.5, 116.1, 77.6, 73.3, 72.1, 71.8, 21.3; IR

(film) $\nu = 2977, 1541, 1474, 1367, 1085, 924 \text{ cm}^{-1}$; $[\alpha]_D^{20} = +5.0^\circ$ (c 1.2, chloroform).

(10) 1,3,5-Tribromo-2-(allyloxymethyl)-4,6-bis(2',2'-bis(methoxycarbonyl)pent-4'-enyl)benzene (13). Following procedure A, methyl 2-(2'-propenyl)malonate **4** (2.71 g, 15.75 mmol) in THF (10 mL) was treated sequentially with NaH (0.60 g, 80% in paraffin oil, 20.00 mmol, 0.5 h) in THF (30 mL) and **10** (3.00 g, 5.25 mmol, 9.5 h) in THF (10 mL) to give **13** (2.67 g, 68%) as a white solid; mp: 63°C (ether-hexane); ^1H NMR (300 MHz, CDCl_3) δ 6.03-5.70 (m, 3H), 5.31 (d, $J = 17.02 \text{ Hz}$, 1H), 5.19 (d, $J = 8.76 \text{ Hz}$, 1H), 5.15-4.95 (m, 4H), 4.89 (s, 2H), 4.17-3.91 (m, 6H), 3.60 (s, 12H), 2.70 (d, $J = 7.00 \text{ Hz}$, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.9, 138.3, 136.7, 134.5, 133.4, 131.3, 129.8, 118.6, 117.3, 74.2, 71.7, 58.0, 52.4, 42.3, 39.9; IR (KBr) $\nu = 2952, 1736, 1639, 1437, 1206, 1135, 1086, 994, 924, 849 \text{ cm}^{-1}$; MS (70 eV, EI) m/z (%): 675 ($\text{M}^+ - \text{Br}$ ($2 \times ^{81}\text{Br}$), 56.32), 673 ($\text{M}^+ - \text{Br}$ ($1 \times ^{81}\text{Br}$, $1 \times ^{79}\text{Br}$), 100.00), 671 ($\text{M}^+ - \text{Br}$ ($2 \times ^{79}\text{Br}$), 51.93); Anal. calcd for $\text{C}_{28}\text{H}_{33}\text{O}_9\text{Br}_3$: C, 44.65; H, 4.42. Found: C, 44.67; H, 4.31.

(11) 1,3,5-Tribromo-2-(allyloxymethyl)-4,6-bis(2',2',5'-tris(methoxycarbonyl) pent-4-enyl)benzene (15). Following procedure A, **14** (1.12 g, 4.87 mmol) in THF (10 mL) was treated sequentially with NaH (0.22 g, 60% in paraffin oil, 5.50 mmol, 10 min) in THF (15 mL) and **10** (1.20 g, 2.10 mmol, 3.3 h) in THF (10 mL) to give **15** (1.13 g, 62%) as a colorless liquid; ^1H NMR (300 MHz, CDCl_3) δ 6.90 (dt, $J = 15.68$ and 7.17 Hz , 2H), 6.08-5.88 (m, 1H), 5.77 (d, $J = 15.60 \text{ Hz}$, 2H), 5.31 (d, $J = 17.20 \text{ Hz}$, 1H), 5.20 (d, $J = 10.34 \text{ Hz}$, 1H), 4.86 (s, 2H), 4.09 (s, 2H), 4.06 (s, 4H), 3.69 (s, 6H), 3.66 (s, 12H), 2.80 (d, $J = 7.23 \text{ Hz}$, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.4, 166.3, 143.8, 137.9, 137.1, 134.4, 131.3, 130.1, 123.7, 117.4, 74.2, 71.8, 57.3, 52.8, 51.5, 42.2, 37.5; IR (KBr) $\nu = 2999, 2953, 1729, 1657, 1435, 1255, 1083, 1035, 984 \text{ cm}^{-1}$; MS (70 eV, EI) m/z (%): 791 ($\text{M}^+ -$

Br ($2 \times {}^{81}\text{Br}$), 54.67), 789 ($\text{M}^+ - \text{Br}$ ($1 \times {}^{81}\text{Br}$, $1 \times {}^{79}\text{Br}$), 100.00), 787 ($\text{M}^+ - \text{Br}$ ($2 \times {}^{79}\text{Br}$), 51.80); Anal. calcd for $\text{C}_{32}\text{H}_{37}\text{O}_{13}\text{Br}_3$: C, 44.21; H, 4.29. Found: C, 44.59; H, 4.50.

(12) 1,3,5-Tribromo-2,4-bis(allyloxymethyl)-6-(N-allyl-N-(*p*-toluenesulphonyl)amino methyl)benzene (19). To a suspension of NaH (0.11 g, 60% in paraffin oil, 2.75 mmol) in THF (15 mL) was added **16** (0.51 g, 2.42 mmol) in THF (5 mL) slowly through a dropping funnel. After the addition, the mixture was stirred for additional 30 min at room temperature. Then, **11** (1.10 g, 2.01 mmol) in THF (5 mL) was added. After stirring for 1 h at room temperature, DMF (10 mL) was added. The reaction was quenched with water after stirring for additional 4.5 h at room temperature, extracted with ether, and washed with brine. The combined organic extracts were dried over MgSO_4 and evaporated. The crude product was further purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 20:2:1) to give **19** (1.28 g, 94%) as a white solid; mp: 88–89°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.68 (d, $J = 8.07$ Hz, 2H), 7.28 (d, $J = 8.07$ Hz, 2H), 6.08–5.85 (m, 2H), 5.60–5.40 (m, 1H), 5.31 (d, $J = 17.16$ Hz, 2H), 5.19 (d, $J = 10.34$ Hz, 2H), 5.05–4.65 (m, 8H), 4.06 (d, $J = 5.72$ Hz, 4H), 3.67 (d, $J = 5.93$ Hz, 2H), 2.42 (s, 3H), 5.19 (d, $J = 10.34$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.4, 137.4, 135.6, 134.4, 134.2, 133.9, 131.4, 130.8, 129.6, 127.5, 117.5, 116.6, 73.3, 71.8, 54.5, 50.6, 21.6; IR (KBr) $\nu = 1539, 1352, 1335, 1167, 1087, 1060, 925\text{ cm}^{-1}$; MS (70 eV, EI) m/z (%): 624 ($\text{M}^+ - \text{C}_3\text{H}_4\text{O}$ ($3 \times {}^{81}\text{Br}$), 8.92), 622 ($\text{M}^+ - \text{C}_3\text{H}_4\text{O}$ ($2 \times {}^{81}\text{Br}$, $1 \times {}^{79}\text{Br}$) 23.36), 620 ($\text{M}^+ - \text{C}_3\text{H}_4\text{O}$ ($1 \times {}^{81}\text{Br}$, $2 \times {}^{79}\text{Br}$), 24.21), 618 ($\text{M}^+ - \text{C}_3\text{H}_4\text{O}$ ($3 \times {}^{79}\text{Br}$), 9.09), 597 (100); Anal. calcd for $\text{C}_{25}\text{H}_{28}\text{SO}_4\text{NBr}_3$: C, 44.27; H, 4.16; N, 2.07. Found: C, 44.25; H, 4.19; N, 1.97.

(13) 1,3,5-Tribromo-2,4-bis(allyloxymethyl)-6-(2',2',5'-tris(methoxycarbonyl)-pent-

4'-enyl)benzene (20). Following procedure A, **14** (0.75 g, 3.26 mmol) in THF (5 mL) was treated sequentially with NaH (0.13 g, 60% in paraffin oil, 3.26 mmol, 30 min) in THF (15 mL) and **11** (0.90 g, 1.64 mmol, 4.5 h) in THF (5 mL) to give **20** (1.08 g, 94%) as a colorless liquid; ^1H NMR (300 MHz, CDCl_3) δ 6.83 (dt, J = 15.60 and 7.26 Hz, 1H), 5.96-5.84 (m, 2H), 5.66 (d, J = 15.60 Hz, 1H), 5.26 (d, J = 15.71 Hz, 2H), 5.14 (d, J = 10.37 Hz, 2H), 4.83 (s, 4H), 4.03 (s, 2H), 4.02 (s, 4H), 3.62 (s, 3H), 3.59 (s, 6H), 2.76 (d, J = 7.32 Hz, 2H); IR (KBr) ν = 2952, 1732, 1536, 1435, 1268, 1198, 1170, 1084, 987 cm^{-1} ; MS (70 eV, EI) m/z (%): 619 ($\text{M}^+ - \text{Br}$ ($2 \times ^{81}\text{Br}$), 52.74), 617 ($\text{M}^+ - \text{Br}$ ($1 \times ^{81}\text{Br}$, $1 \times ^{79}\text{Br}$), 100.00), 615 ($\text{M}^+ - \text{Br}$ ($2 \times ^{79}\text{Br}$), 53.40); Anal. calcd for $\text{C}_{25}\text{H}_{29}\text{O}_8\text{Br}_3$: C, 43.07; H, 4.19. Found: C, 43.74; H, 4.40.

(14) 1,3,5-Tribromo-2,4-bis(allyloxymethyl)-6-((3'-phenyl-2'-propenoxy)methyl)-benzene (21). Following procedure C, cinamyl alcohol (0.49 g, 3.66 mmol) in THF (15 mL) was treated sequentially with NaH (0.173 g, 55% in paraffin oil, 3.96 mmol, 30 min) in THF (5 mL) and **11** (1.00 g, 1.82 mmol) in THF (5 mL) to give **21** (0.61 g, 56%) as a white solid; mp: 60-61°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.44-7.20 (m, 5H), 6.67 (d, J = 15.90 Hz, 1H), 6.53 (dt, J = 15.90 and 6.00 Hz, 1H), 6.10-5.90 (m, 2H), 5.36 (dd, J = 17.4 and 1.70 Hz, 2H), 5.23 (d, J = 9.90 Hz, 2H), 4.99 (s, 2H), 4.93 (s, 4H), 4.29 (d, J = 5.70 Hz, 2H), 4.12 (d, J = 5.70 Hz, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.2, 136.5, 134.4, 132.8, 130.7, 130.6, 128.5, 127.6, 126.4, 125.6, 117.6, 73.3, 71.8, 71.4; IR (KBr) ν = 1541, 1475, 1344, 1122, 1087, 936 cm^{-1} ; MS (70 eV, EI) m/z (%): 465 ($\text{M}^+ - \text{C}_3\text{H}_6\text{O}$ ($2 \times ^{81}\text{Br}$), 5.71), 463 ($\text{M}^+ - \text{C}_3\text{H}_6\text{O}$ ($1 \times ^{81}\text{Br}$, $1 \times ^{79}\text{Br}$), 10.30), 461 ($\text{M}^+ - \text{C}_3\text{H}_6\text{O}$ ($2 \times ^{79}\text{Br}$), 5.01); Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{O}_3\text{Br}_3$: C, 47.95; H, 4.19. Found: C, 48.03; H, 4.33.

(15) 1,3,5-Tribromo-2,4-bis(allyloxymethyl)-6-(but-3'-enyl)benzene (18). Following procedure B, allyl magnesium bromide (0.4 M, 14 mL) was treated with **11** (2.00 g, 3.65 mmol) in THF (15 mL) to give **18** (1.23 g, 66%) as a colorless liquid; ^1H NMR (300 MHz, CDCl_3) δ 6.08-5.85 (m, 3H), 5.35 (d, $J = 17.44$ Hz, 2H), 5.22 (d, $J = 10.35$ Hz, 2H), 5.12 (d, $J = 16.98$ Hz, 2H), 5.03 (d, $J = 10.38$ Hz, 2H), 4.93 (s, 4H), 4.13 (d, $J = 5.41$ Hz, 4H), 3.29-3.10 (m, 2H), 2.40-2.16 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.4, 137.1, 136.8, 134.5, 129.1, 128.0, 117.6, 115.2, 73.5, 71.9, 38.3, 31.5; IR (KBr) $\nu = 3078, 2849, 1641, 1538, 1454, 1367, 1086, 990, 921\text{ cm}^{-1}$; MS (70 eV, EI) m/z (%): 359 ($\text{M}^+ - \text{C}_3\text{H}_5 - 2 \times \text{C}_3\text{H}_4\text{O}$ ($3 \times ^{81}\text{Br}$), 19.16), 357 ($\text{M}^+ - \text{C}_3\text{H}_5 - 2 \times \text{C}_3\text{H}_4\text{O}$ ($2 \times ^{81}\text{Br}, 1 \times ^{79}\text{Br}$), 58.30), 355 ($\text{M}^+ - \text{C}_3\text{H}_5 - 2 \times \text{C}_3\text{H}_4\text{O}$ ($1 \times ^{81}\text{Br}, 2 \times ^{79}\text{Br}$), 60.13), 353 ($\text{M}^+ - \text{C}_3\text{H}_5 - 2 \times \text{C}_3\text{H}_4\text{O}$ ($3 \times ^{79}\text{Br}$), 22.99), 105 (100.00); Anal. calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2\text{Br}_3$: C, 42.47; H, 4.16. Found: C, 42.70; H, 4.22.

(16) 1,3,5-Tribromo-2,4-bis(allyloxymethyl)-6-(but-3'-enoxymethyl)benzene (22). Following procedure C, 3-buten-1-ol **17** (0.29 g, 4.02 mmol) in THF (2 mL) was treated sequentially with NaH (0.18 g, 60% in paraffin oil, 4.50 mmol, 30 min) in THF (4 mL) and **11** (1.10 g, 2.01 mmol, 12 h) in THF (2 mL) to give **22** (0.89 g, 82%) as a white solid; mp: 38°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 6.05-5.75 (m, 3H), 5.33 (d, $J = 17.13$ Hz, 2H), 5.20 (d, $J = 11.16$ Hz, 2H), 5.09 (d, $J = 17.33$ Hz, 1H), 4.99 (d, $J = 7.08$ Hz, 1H), 4.91 (s, 6H), 4.10 (d, $J = 5.62$ Hz, 4H), 3.60 (t, $J = 6.73$ Hz, 2H), 2.45-2.28 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.2, 135.0, 134.5, 130.7, 117.5, 116.3, 73.9, 73.3, 71.9, 70.2, 34.1; IR (KBr) $\nu = 1540, 1353, 1092, 923\text{ cm}^{-1}$; MS (70 eV, EI) m/z (%): 357 ($\text{M}^+ - \text{C}_4\text{H}_6\text{O} - 2 \times \text{C}_3\text{H}_4\text{O}$ ($3 \times ^{81}\text{Br}$), 33.36), 355 ($\text{M}^+ - \text{C}_4\text{H}_6\text{O} - 2 \times \text{C}_3\text{H}_4\text{O}$ ($2 \times ^{81}\text{Br}, 1 \times ^{79}\text{Br}$), 98.12), 353 ($\text{M}^+ - \text{C}_4\text{H}_6\text{O} - 2 \times \text{C}_3\text{H}_4\text{O}$ ($1 \times ^{81}\text{Br}, 2 \times ^{79}\text{Br}$), 100.00), 351 ($\text{M}^+ - \text{C}_4\text{H}_6\text{O} - 2$

$\times \text{C}_3\text{H}_4\text{O}$ ($3 \times {}^{79}\text{Br}$), 34.01); Anal. calcd for $\text{C}_{19}\text{H}_{23}\text{O}_3\text{Br}_3$: C, 42.33; H, 4.30. Found: C, 42.26; H, 4.20.

Pd(0)-Catalyzed Cyclization Reaction

(1) Synthesis of 23. Typical Procedure (Conditions B). To a degassed solution of **5** (200 mg, 0.23 mmol), K_2CO_3 (190 mg, 1.38 mmol), and PPh_3 (24 mg, 0.092 mmol) in CH_3CN (4 mL) was added $\text{Pd}(\text{OAc})_2$ (5.2 mg, 0.023 mmol) under Ar, the reaction mixture was stirred under reflux for 32 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 5:1). The residue was passed through a short column of silica gel (eluent: ethyl acetate) to remove the catalyst and inorganic salts. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford compound **23** (125 mg, 87%) as a white solid: mp 176-7°C (ethyl acetate-hexane); ^1H NMR (300 MHz, CDCl_3) δ 5.38 (s, 3H), 5.01 (s, 3H), 3.67 (s, 18H), 3.35 (s, 6H), 3.10 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 171.6, 138.66, 135.6, 129.86, 116.9, 54.9, 53.0, 38.2, 32.4; IR (KBr) ν = 2957, 1738, 1438, 1312, 1261, 1200, 1180, 1075, 1055, 914 cm^{-1} ; MS (70 eV, EI) m/z (%): 624 (M^+ , 99.79), 445 (100.00); Anal. calcd for $\text{C}_{33}\text{H}_{36}\text{O}_{12}$: C, 63.45; H, 5.81. Found: C, 63.21; H, 5.71.

(2) 1,5,9-Trimethylene-3,7,11-trioxa-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotri-phenylene (24) (Conditions B). A degassed solution of compound **13** (200 mg, 0.38 mmol), Cs_2CO_3 (248 mg, 0.76 mmol), PPh_3 (40 mg, 0.153 mmol), and $\text{Pd}(\text{OAc})_2$ (8.5 mg, 0.038 mmol) in CH_3CN (4 mL) was stirred under reflux for 48 h. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate =

20:1) to afford compound **24** (77 mg, 72%) as a white solid: mp 107-8°C (ether-hexane); ¹H NMR (300 MHz, CDCl₃) δ 5.31 (s, 3H), 4.91 (s, 3H), 4.78 (s, 6H), 4.54 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 137.7, 134.0, 130.3, 114.1, 70.0, 66.0; IR (KBr) ν = 3095, 2975, 2846, 1619, 1447, 1108, 966, 881, 810; cm⁻¹; MS (70 eV, EI) m/z (%): 283 (M⁺+1, 14.10), 282 (M⁺, 100.00); Anal. calcd for C₁₈H₁₈O₃: C, 76.57; H, 6.43. Found: C, 76.57; H, 6.42.

(3) **1,5,9-Trimethylene-2,6,10-trimethyl-3,7,11-trioxa-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene (25) (Conditions B).** A degassed solution of compound **9** (200 mg, 0.35 mmol), K₂CO₃ (292 mg, 2.12 mmol), PPh₃ (37 mg, 0.141 mmol), and Pd(OAc)₂ (7.9 mg, 0.035 mmol) in CH₃CN (4 mL) was stirred under reflux for 54 h. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford compound **25** (94 mg, 82%) as a white solid: mp 124-5°C (hexane); (S*,S*,S*)-**25**: ¹H NMR (300 MHz, CDCl₃) δ 5.33 (d, *J* = 1.64 Hz, 3H), 4.89 (d, *J* = 14.07 Hz, 3H), 4.81 (d, *J* = 1.64 Hz, 3H), 4.79-4.72 (m, 3H), 4.49 (d, *J* = 14.07 Hz, 3H), 1.40 (d, *J* = 6.33 Hz, 9H); the following signals are discernible for (R*,R*,S*)-**25**: ¹H NMR (300 MHz, CDCl₃) δ 5.29-5.20 (m, 3H), 5.00-4.30 (m, 12H), 1.37-1.25 (m, 9H); IR (KBr) ν = 2979, 2828, 1620, 1258, 1105, 1064, 903 cm⁻¹; MS (70 eV, EI) m/z (%): 324 (M⁺, 45.81), 281 (100.00); Anal. calcd for C₂₁H₂₄O₃: C, 77.75; H, 7.46. Found: C, 77.80; H, 7.34.

(4) **1,5,9-Trimethylene-2(S),6(S),10(S)-trimethyl-3,7,11-trioxa-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene (S,S,S)-25 (Conditions B).** A degassed solution of compound (S,S,S)-**9** (150 mg, 0.27 mmol), K₂CO₃ (219 mg, 1.59 mmol), PPh₃ (28 mg, 0.107 mmol), and Pd(OAc)₂ (5.9 mg, 0.027 mmol) in CH₃CN (3 mL) was stirred under

reflux for 48 h. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford compound **(S,S,S)-25** (71 mg, 83%) as a white solid: mp 153–4°C (petroleum ether); ^1H NMR (300 MHz, CDCl_3) δ 5.30 (d, J = 1.6 Hz, 3H), 5.00 (d, J = 14.05 Hz, 3H), 4.81 (d, J = 1.6 Hz, 3H), 4.72 (q, J = 6.6 Hz, 3H), 4.40 (d, J = 14.05 Hz, 3H), 1.38 (d, J = 6.50 Hz, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.3, 134.4, 130.4, 114.1, 75.6, 65.1, 23.3; IR (KBr) ν = 2967, 2828, 1620, 1610, 1066, 895 cm^{-1} ; $[\alpha]_D^{20}$ = -260° (c 1.0, chloroform).

(5) 1,5,9-Trimethylene-2,10-dimethyl-3,7,11-trioxa-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene (26) (Conditions B). A degassed solution of compound **12** (200 mg, 0.36 mmol), K_2CO_3 (300 mg, 2.17 mmol), PPh_3 (38 mg, 0.145 mmol), and $\text{Pd}(\text{OAc})_2$ (8.1 mg, 0.036 mmol) in CH_3CN (4 mL) was stirred under reflux for 54 h. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 35:1) to afford compound **26** (80 mg, 71%) as a white solid; mp: 103–104°C (hexane); **(S*,S*)-26**: ^1H NMR (300 MHz, CDCl_3) δ 5.27–5.21 (m, 3H), 5.02–4.20 (m, 13H), 1.31 (d, J = 2.50 Hz, 3H), 1.29 (d, J = 2.50 Hz, 3H); the following signals are discernible for **(R*,S*)-26**: ^1H NMR (300 MHz, CDCl_3) δ 5.33–5.21 (m, 3H), 5.02–4.20 (m, 13H), 1.40–1.30 (m, 6H); IR (KBr) ν = 2973, 2835, 1620, 1260, 1109, 1064, 914, 899, 830 cm^{-1} ; MS (70 eV, EI) m/z (%): 310 (M^+ , 73.08), 165 (100.00); Anal. calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3$: C, 77.39; H, 7.14. Found: C, 77.34; H, 7.21.

(6) 1,5,9-Trimethylene-2(S),10(S)-dimethyl-3,7,11-trioxa-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene (S,S)-26. (Conditions B). A degassed solution of compound **(S,S)-12** (200 mg, 0.36 mmol), K_2CO_3 (300 mg, 2.17 mmol), PPh_3 (38 mg, 0.145 mmol), and $\text{Pd}(\text{OAc})_2$ (8.1 mg, 0.036 mmol) in CH_3CN (4 mL) was stirred under reflux for 46 h.

The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 35:1) to afford compound (S,S)-**26** (81 mg, 72%) as a white solid; mp: 142-3°C (petroleum ether); ¹H NMR (300 MHz, CDCl₃) δ 5.35-5.27 (m, 3H), 5.10-4.95 (m, 3H), 4.92-4.80 (m, 3H), 4.78-4.37 (m, 7H). 1.37 (d, *J* = 2.6 Hz, 3H), 1.35 (d, *J* = 2.7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 143.5, 138.1, 135.0, 134.1, 130.9, 130.8, 130.5, 114.5, 114.1, 75.8, 75.8, 70.0, 66.2, 65.2, 23.4; IR (KBr) ν = 2971, 2830, 1448, 1370, 1259, 1224, 1105, 1064, 895 cm⁻¹; [α]_D²⁰ = -198° (c 1.0, chloroform).

(7) 1,5,9-Trimethylene-7-oxa-3,3,11,11-tetrakis(methoxycarbonyl)-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene (27). (Conditions B). A degassed solution of compound **13** (200 mg, 0.27 mmol), K₂CO₃ (220 mg, 1.59 mmol), PPh₃ (28 mg, 0.11 mmol), and Pd(OAc)₂ (6.0 mg, 0.03 mmol) in CH₃CN (4 mL) was stirred under reflux for 48 h. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to afford compound **27** (30 mg, 22%) as a white solid: mp 131°C (ether-hexane); ¹H NMR (300 MHz, CDCl₃) δ 5.45 (s, 1H), 5.38 (s, 1H), 5.34 (s, 1H), 5.22 (s, 1H), 5.15 (s, 1H), 4.75 (s, 1H), 4.65 (s, 2H), 4.50 (s, 2H), 3.68 (s, 6H), 3.60 (s, 6H), 3.42 (s, 2H), 3.39 (s, 2H), 3.13 (s, 2H), 3.09 (s, 1H); IR (KBr) ν = 1737, 1435, 1249, 1216, 1178, 1100, 1073, 1055, 916; cm⁻¹; MS (70 eV, EI) *m/z* (%): 510 (M⁺, 19.69), 84 (100.00); Anal. calcd for C₂₈H₃₀O₉: C, 65.87; H, 5.92. Found: C, 65.93; H, 5.90.

(8) 1,5,9-Trimethylene-3,11-dioxa-7-(toluene-4-sulfon-yl)-7-aza-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene (28). (Conditions B). A degassed solution of compound **19** (200 mg, 0.30 mmol), K₂CO₃ (244 mg, 1.77 mmol), PPh₃ (31 mg, 0.118 mmol), and Pd(OAc)₂ (6.6 mg, 0.03 mmol) in CH₃CN (4 mL) was stirred under reflux for 47 h. The residue was purified by flash column chromatography on silica gel (petroleum

ether/ethyl acetate = 5:1) to afford compound **28** (64 mg, 50%) as a white solid: mp 212°C (ethyl acetate-hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.35 (d, J = 8.27 Hz, 2H), 7.04 (d, J = 8.27 Hz, 2H), 5.42 (s, 1H), 5.40 (s, 1H), 5.30 (s, 1H), 5.04 (s, 1H), 4.87 (s, 1H), 4.85 (s, 1H), 4.71 (s, 2H), 4.64 (s, 2H), 4.61 (s, 2H), 4.53 (s, 2H), 4.47 (s, 2H), 4.31 (s, 2H), 2.28 (s, 3H); IR (KBr) ν = 1333, 1163, 1114, 1092, 914, 670 cm^{-1} ; MS (70 eV, EI) m/z (%): 435 (M^+ , 100.00), 436 ($\text{M}^+ + 1$, 21.74); Anal. calcd for $\text{C}_{25}\text{H}_{25}\text{SO}_4\text{N}$: C, 68.94; H, 5.79; N, 3.22. Found: C, 68.84; H, 5.64; N, 3.06.

(9) Synthesis of 29. Typical Procedure (Conditions A). A degassed solution of compound **20** (200 mg, 0.29 mmol), Cs_2CO_3 (187 mg, 0.57 mmol), PPh_3 (30 mg, 0.115 mmol), and $\text{Pd}(\text{OAc})_2$ (6.4 mg, 0.03 mmol) in CH_3CN (4 mL) was stirred under reflux for 46 h. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford compound **29** (46 mg, 35%) as a white solid: mp 166-7°C (dichloromethane-hexane); ^1H NMR (300 MHz, CDCl_3) δ 5.58 (s, 1H), 5.45 (s, 1H), 5.30 (s, 1H), 5.22 (s, 1H), 4.85 (s, 1H), 4.70 (s, 2H), 4.68 (s, 2H), 4.55 (s, 2H), 4.50 (s, 2H), 3.78 (s, 5H), 3.60 (s, 6H), 3.45 (s, 2H); IR (KBr) ν = 2950, 1737, 1713, 1613, 1433, 1199, 1173, 1106, 1052 cm^{-1} ; MS (70 eV, EI) m/z (%): 454 (M^+ , 78.15), 422 (100.00); HRMS calcd for $\text{C}_{25}\text{H}_{26}\text{O}_8$: 454.16277. found: 454.16776.

(10) 5,9-Dimethylene-1-benzylidene-3,7,11-trioxa-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene (30) and 10-bromo-4,8-dimethylene-9-(3'-phenyl-2-propenyl-methyl)-2,6-dioxa-1,2,3,4,5,6,7,8-octahydrophenanthrene (31). (Conditions B). A degassed solution of compound **21** (200 mg, 0.33 mmol), K_2CO_3 (276 mg, 2.00 mmol), PPh_3 (35 mg, 0.13 mmol), and $\text{Pd}(\text{OAc})_2$ (8 mg, 0.036 mmol) in CH_3CN (4 mL) was stirred under reflux for 48 h. The residue was purified by flash column chromatography

on silica gel (petroleum ether/ethyl acetate = 15:1) to afford compound **30** (60 mg, 50%) and **31** (16 mg, 11%). **30**: white solid; mp: 193-194°C (dichloromethane-hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.50-7.20 (m, 5H), 6.26 (t, J = 2.30 Hz, 1H), 5.37 (t, J = 1.90 Hz, 1H), 5.33 (t, J = 1.7 Hz, 1H), 5.00-4.80 (m, 8H), 4.69 (s, 2H), 4.61 (s, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.9, 137.7, 135.7, 135.4, 133.9, 133.5, 132.4, 131.7, 130.8, 130.3, 130.0, 129.2, 128.4, 127.6, 114.1, 114.0, 69.9, 69.8, 67.6, 66.1, 65.9, 65.0; IR (KBr) ν = 2829, 1448, 1095, 887, 693 cm^{-1} ; MS (70 eV, EI) m/z (%): 358 (M^+ , 65.61), 268 (100.00); Anal. calcd for $\text{C}_{24}\text{H}_{22}\text{O}_3$: C, 80.42; H, 6.19. Found: C, 80.12; H, 6.60. **31**: white solid; mp: 116-117°C (ether-hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.10 (m, 5H), 6.60 (d, J = 15.88 Hz, 1H), 6.32 (dt, J = 15.89, 5.50 Hz, 1H), 5.66 (s, 1H), 5.39 (s, 1H), 5.28 (s, 1H), 4.88 (s, 1H), 4.79 (s, 2H), 4.64 (d, J = 1.22 Hz, 4H), 4.49 (s, 2H), 4.25 (d, J = 6.11 Hz, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.9, 136.5, 136.3, 136.2, 135.4, 133.7, 132.9, 132.1, 128.5, 127.7, 126.5, 126.4, 125.7, 124.9, 117.5, 115.2, 71.4, 70.7, 70.1, 70.0, 69.7, 65.3; IR (KBr) ν = 2843, 1449, 1354, 1114, 1073, 963, 927, 688 cm^{-1} ; MS (70 eV, EI) m/z (%): 320 ($\text{M}^+ - \text{C}_9\text{H}_{10}\text{O}$ (^{79}Br), 11.44), 322 ($\text{M}^+ - \text{C}_9\text{H}_{10}\text{O}$ (^{81}Br), 12.40), 237 (100.00); Anal. calcd for $\text{C}_{24}\text{H}_{23}\text{O}_3\text{Br}$: C, 65.61; H, 5.28. Found: C, 65.52; H, 5.60.

(11) 1-Methylene-5,9-bis((methoxycarbonyl)methylene)-3-oxa-7,7,11,11-tetra(methoxycarbonyl)-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene (32) (Conditions A).

A degassed solution of compound **15** (200 mg, 0.23 mmol), Cs_2CO_3 (150 mg, 0.46 mmol), PPh_3 (24 mg, 0.092 mmol), and $\text{Pd}(\text{OAc})_2$ (6.4 mg, 0.023 mol%) in CH_3CN (4 mL) was stirred under reflux for 50 h. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to afford compound **32** (45 mg, 31%) as a white solid: mp 96-7°C; ^1H NMR (300 MHz, CDCl_3) δ 5.79 (t, J = 2.22 Hz, 1H), 5.40

(t, $J = 2.34$ Hz, 1H), 5.35 (s, 1H), 5.11 (s, 1H), 4.55 (s, 2H), 4.45 (s, 2H), 3.75-3.60 (m, 16H), 3.51 (s, 6H), 3.32 (s, 4H); IR (KBr) $\nu = 2953, 1737, 1715, 1619, 1436, 1259, 1196, 1174, 1075, 1052, 788$ cm^{-1} ; MS (70 eV, EI) m/z (%): 626 (M^+ , 29.70), 119 (100.00); HRMS calcd for $\text{C}_{32}\text{H}_{34}\text{O}_8$: 626.19995; found: 626.19849.

(12) 1,4,8-Trimethylene-6,10-dioxo -1,2,3,4,5,6,7,8,9,10,11-undecahydrocyclopenta [l]phenanthrene (33). (Conditions B). A degassed solution of compound **18** (150 mg, 0.29 mmol), K_2CO_3 (244 mg, 1.77 mmol), PPh_3 (31 mg, 0.118 mmol), and $\text{Pd}(\text{OAc})_2$ (6.6 mg, 0.029 mol%) in CH_3CN (3.5 mL) was stirred under reflux for 46 h. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford compound **33** (48 mg, 61%) as a white solid: mp 127-8°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 5.48 (s, 1H), 5.42 (s, 1H), 5.27 (s, 1H), 5.25 (s, 1H), 5.08 (s, 1H), 5.06 (s, 2H), 5.02 (s, 1H), 4.93 (s, 2H), 4.52 (s, 2H), 4.35 (s, 2H), 3.20 – 3.09 (m, 2H), 2.90 – 2.75 (m, 2H); IR (KBr) $\nu = 2963, 2822, 1625, 1443, 1261, 1104, 1022, 801$ cm^{-1} ; MS (70 eV, EI) m/z (%): 266 (M^+ , 100.00), 267 ($M^+ + 1$, 22.93); Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$: C, 81.17; H, 6.81. Found: C, 81.15; H, 6.80.

(13) 4,8,13-Trimethylene-2,6,10-trioxa-1,2,3,4,5,6,7,8,9,10,11,12,13-tridecahydro-cyclohepta [l]phenanthrene (34). (Conditions A). A degassed solution of compound **22** (100 mg, 0.19 mmol), Cs_2CO_3 (121 mg, 0.37 mmol), PPh_3 (19 mg, 0.073 mmol), and $\text{Pd}(\text{OAc})_2$ (4.2 mg, 0.019 mol%) in CH_3CN (2.5 mL) was stirred under reflux for 44 h. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford compound **34** (27 mg, 49%) as a white solid: mp 119°C (hexane); ^1H NMR (300 MHz, CDCl_3) δ 5.48 (s, 1H), 5.39 (s, 1H), 5.37 (s, 1H), 5.24 (s, 1H), 5.03-4.90 (m, 3H), 4.87-4.70 (m, 5H), 4.56 (s, 2H), 4.45 (s, 2H), 4.06 (s,

2H), 2.55-2.47 (m, 2H); IR (KBr) ν = 2932, 2849, 1635, 1108, 1091, 938, 907 cm^{-1} ;
MS (70 eV, EI) m/z (%): 296 (M^+ , 100.00), 297 ($M^+ + 1$, 14.80); Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{O}_3$: C, 77.00; H, 6.80. Found: C, 77.12; H, 6.75.

References:

1. Engman, L.; Hellberg, J. S. E. *J. Organomet. Chem.* **1985**, 296, 357.
2. Oppolzer, W.; Gaudin, J. M.; Birkinshaw, T. N. *Tetrahedron Lett.* **1988**, 29, 4705.
3. Padwa, A.; Murphree, S. S.; Ni, Z.; Watterson, S. H. *J. Org. Chem.* **1996**, 61, 3829.
4. House, H. O.; Liang, W. C.; Week, P. D. *J. Org. Chem.* **1974**, 39, 3102.
5. Balmer, E.; Germain, A.; Jackson, W. P.; Lygo, B. *J. Chem. Soc., Perkin Trans. 1* **1993**, 399.
6. Coulson, D. R. *Inorg. Synth.* **1972**, 13, 121.
7. Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. organomet. Chem.* **1974**, 65, 253.
8. Anthony, J. E.; Khan, S. I.; Rubin, Y. *Tetrahedron Lett.* **1997**, 38, 3499

Figure 1. ORTEP diagram of the molecular structure of compound **29**

Fig 2. ^1H - ^1H NOESY data of compound **32**