Supporting Information

Poly-oxygenated Tricyclobutabenzenes via Repeated [2+2] Cycloaddition of Benzyne and Ketene Silyl Acetal

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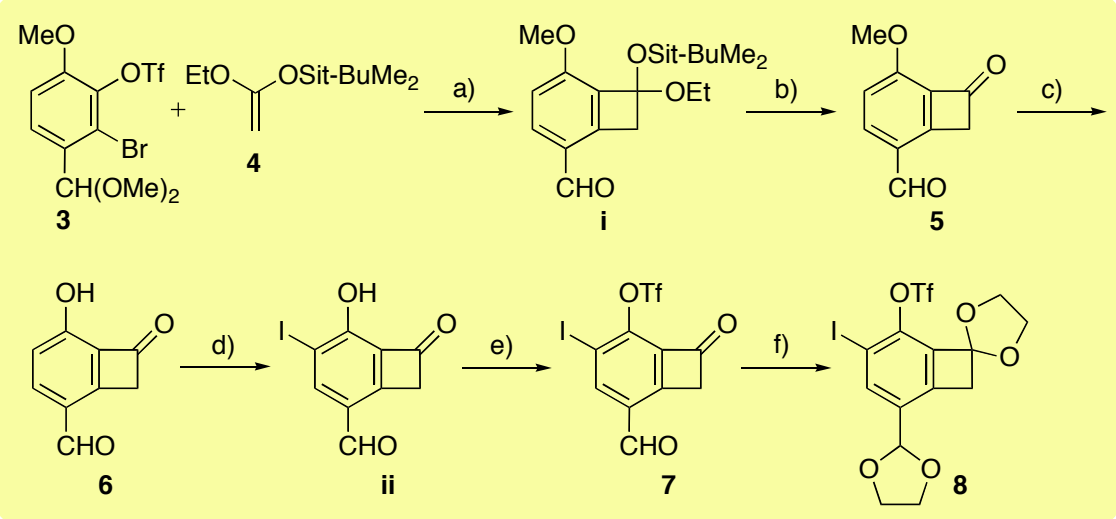
General Experimental Procedures

Ethereal solvents (anhydrous; *Kanto Chemical Co., Inc.*) were used as received. For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F_{254}, Art 5715, 0.25 mm) were used. For flash column chromatography, silica gel 60 (Merck Art 7734, 70–230 mesh) was used. Silica gel preparative TLC (PTLC) was performed on Merck silica gel 60 PF_{254} (Art 7747).

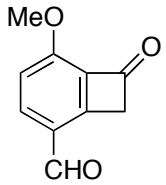
Melting point (mp) determinations were performed by using a Yanako MP-S3 instrument and are uncorrected. ^{1}H NMR and ^{13}C NMR were measured on a JEOL JNM lambda-400, and a Bruker DRX-500 spectrometer. Infrared (IR) spectra were recorded on a Perkin Elmer 1600 FT/IR 200 spectrometer.

Scheme 1. Synthesis of iodo-triflate **8** via first [2+2] cycloaddition



Reagents and conditions: a) *n*-BuLi, THF, –78 °C, 5 min; b) aq. HF, CH_3CN, 25 °C, 15 h (**5**: 60% in 2 steps); c) $AlCl_3$, $ClCH_2CH_2Cl$, 60 °C, 13 h; d) $BnMe_3N^+ICl_2^-$, $NaHCO_3$, CH_2Cl_2, r.t., 20 h; e) Tf_2O, pyr, CH_2Cl_2, 0 °C, 5 min; f) ethylene glycol, TsOH, benzene, reflux, 28 h (**8**: 60% in 4 steps).

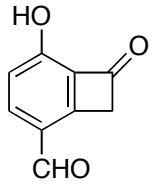
*Synthesis of benzocyclobutenone **5***:
To a mixture of triflate **3** (10.6 g, 25.9 mmol) and ketene silyl acetal **4** (7.80 g, 38.0 mmol) in THF (130 mL) was added *n*-BuLi (1.60 M in hexane, 24 mL, 39 mmol) at –78 °C. After 5 min, the reaction was stopped by adding sat. aq. $NaHCO_3$. Extractive workup (EtOAc) followed by evaporation gave crude cycloadduct **i**.
To a solution of cycloadduct in MeCN (30 mL) was added 46% aq. HF (3.0 mL) at 0 °C. After warmed up to room temperature, the reaction was further stirred for 15 h. After dilution with water, the products were extracted with Et_2O and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 9/1) to afford **5** (2.74 g, 60.1%) as white solids. Recrystallization from hexane–EtOAc gave **5** as colorless needles. Mp 129.2–130.0 °C.



benzocyclobutenone **5**
^{1}H NMR ($CDCl_3$, δ)
4.20 (s, 2H), 4.21 (s, 3H), 6.94 (d, 1H, J = 8.7 Hz), 7.89 (d, 1H, J = 8.7 Hz), 10.0 (s, 1H);
^{13}C NMR ($CDCl_3$, δ)
51.6, 60.8, 117.6, 125.3, 133.2, 138.0, 154.2, 157.3, 183.2, 188.0;
IR (KBr)
3068, 2999, 2956, 2873, 1770, 1693, 1672, 1599, 1564, 1498, 1450, 1435, 1410, 1356, 1304, 1211, 1151, 1057, 1009, 985, 955, 877, 845, 744 cm^{-1};
Anal. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 67.91; H, 4.64.

*Synthesis of phenol **6**:*

To a solution of benzocyclobutene **5** (9.64 g, 54.7 mmol) in 1,2-dichloroethane (220 mL) was added $AlCl_3$ (18.2 g, 136 mmol). After warmed up to 60 °C, and further stirred for 13 h, the reaction mixture was poured into ice water (400 mL). After the mixture was filtered through Celite pad, the products were extracted with EtOAc (X3), washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/acetone = 7/3) to give phenol **6** (7.72 g, 87.0%). Recrystallization from hexane–EtOAc gave **6** as colorless needles. Mp 230.8–231.2 °C.



phenol **6**

^{1}H NMR ($CDCl_3$, δ)

4.16 (s, 2H), 6.92 (d, 1H, J = 8.7 Hz), 7.93 (d, 1H, J = 8.7 Hz), 9.97 (s, 1H), 10.3 (br s, 1H);

^{13}C NMR (acetone-d_6, δ)

52.2, 117.9, 126.2, 135.1, 139.0, 154.6, 155.6, 184.5, 188.9;

IR (KBr)

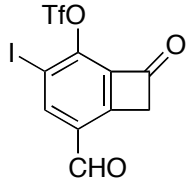
3153, 2861, 2716, 2582, 1774, 1552, 1581, 1500, 1458, 1406, 1315, 1219, 1150, 1048, 1004, 881 cm^{-1};

Anal. Calcd for $C_9H_6O_3$: C, 66.67; H, 3.73. Found: C, 66.85; H, 3.94.

*Synthesis of iodo-triflate **7**:*

To a solution of phenol **6** (7.76 g, 47.9 mmol) in CH_2Cl_2 (500 mL) was added $BnMe_3N^+ICl_2^-$ (19.9 g, 57.2 mmol), followed by $NaHCO_3$ (5.60 g, 66.7 mmol) at room temperature. After 20 h, the reaction mixture was poured into 2 M HCl at 0 °C. The products were extracted with EtOAc (X2), and the combined organic extracts were washed successively with 10% aq. $Na_2S_2O_3$ and brine, dried (Na_2SO_4). Evaporaion of the solvents gave crude iodo-phenol **ii**.

To a solution of iodo-phenol in CH_2Cl_2 (210 mL)–pyridine (53 mL) was slowly added Tf_2O (10 mL, 59 mmol) at 0 °C. After 5 min, the reaction mixture was poured into 2 M HCl. The products were extracted with EtOAc (X2), and the combined organic extracts were successively washed with brine, and dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/acetone = 8/2) to give iodo-triflate **7** (14.5 g, 72.1%). Recrystallization from hexane–EtOAc gave **7** as colorless prisms. Mp 151.8–152.2 °C.



iodo-triflate **7**

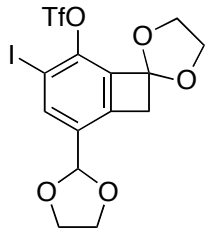
^{1}H NMR ($CDCl_3$, δ)

4.38 (s, 2H), 8.71 (s, 1H), 10.2 (s, 1H);

^{13}C NMR ($CDCl_3$, δ)

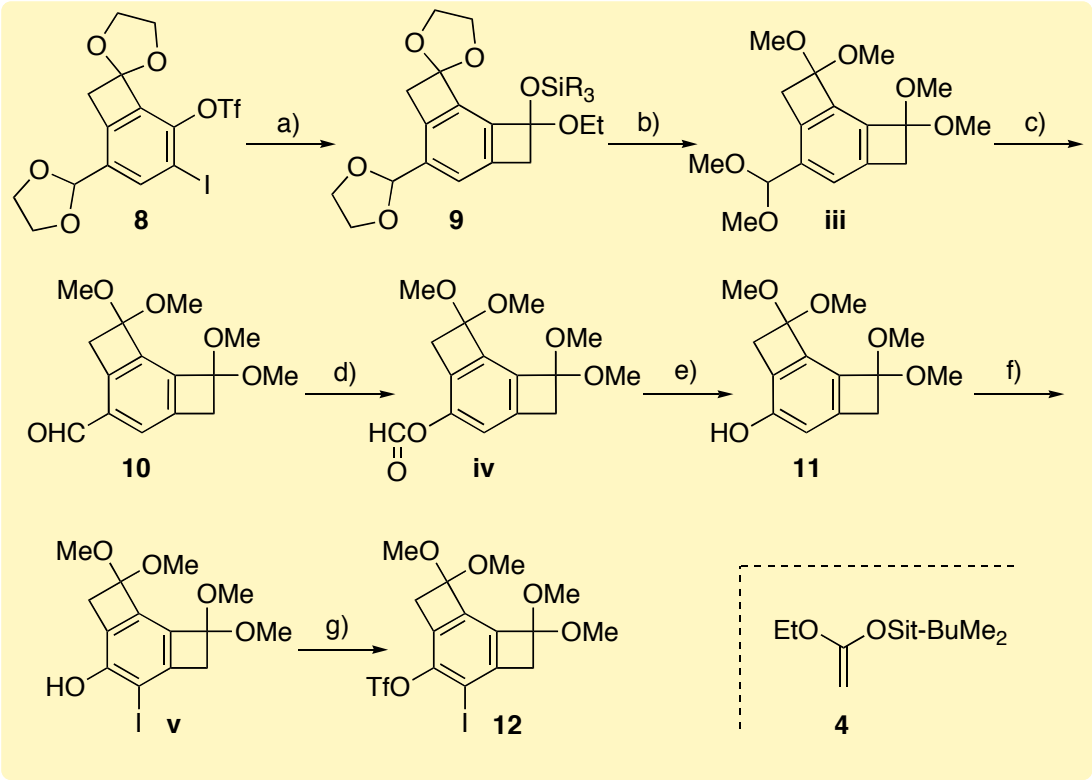
54.4, 90.5, 119.4 (q, J_{C-F} = 319.5 Hz), 133.9, 141.2, 142.0, 149.3, 153.9, 180.7, 189.2;
IR (KBr)
2956, 2867, 1777, 1702, 1695, 1590, 1428, 1235, 1218, 1196, 1125, 1057, 834 cm^{-1};
Anal. Calcd for $C_{10}H_4O_5F_3IS$: C, 28.59; H, 0.96; S, 7.63. Found: C, 28.48; H, 0.80; S, 7.85.

*Synthesis of iodo-triflate **8**:*
To a solution of iodo-triflate **7** (13.4 g, 31.9 mmol) in benzene (106 mL) was added ethyleneglycol (7.10 mL, 127 mmol) and *p*-toluenesulfonic acid monohydrate (1.1 g, 6.5 mmol) at room temperature. The solution was heated at reflux using a Dean–Stark apparatus. After 28 h, the reaction mixture was poured into sat. aq. $NaHCO_3$. The products were extracted with EtOAc (X3), washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 7/3) to give iodo-triflate **8** (15.5 g, 95.7%). Recrystallization from hexane–EtOAc gave **8** as colorless prisms. Mp 81.9–82.2 °C.



iodo-triflate **8**
^{1}H NMR (acetone-d_6, δ)
3.53 (s, 2H), 3.97–4.23 (m, 8H), 5.83 (s, 1H), 8.03 (s, 1H);
^{13}C NMR (acetone-d_6, δ)
49.0, 66.1, 66.4, 87.8, 100.9, 109.8, 119.3 (q, J_{C-F} = 319.9 Hz), 138.1, 140.5, 141.1, 142.1, 144.7;
IR (KBr)
2886, 1589, 1426, 1227, 1130, 1004, 952, 861, 820 cm^{-1};
Anal. Calcd for $C_{14}H_{12}O_7F_3IS$: C, 33.09; H, 2.38; S, 6.31. Found: C, 33.15; H, 2.18; S, 6.08.

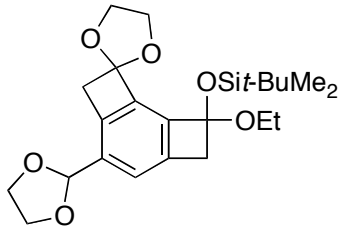
Scheme 2. Synthesis of iodo-triflate **12** via second [2+2] cycloaddition



Reagents and conditions: a) **4**, *n*-BuLi, THF, –78 °C, 5 min (**9**: 70%); b) TsOH, MeOH, r.t., 10 h (**iii**: 93%); c) 0.12 M H_2SO_4, THF, r.t., 5 h (**10**: 97%); d) mCPBA, CH_2Cl_2, 40 °C, 14 h; e) 0.1 M NaOH, 1,4-dioxane, 0 °C → r.t., 42 h (**11**: 76% in 2 steps); f) $BnMe_3N^+ICl_2^-$, *i*-Pr_2NEt, CH_2Cl_2, –78 → –50 °C, 7 h; g) Tf_2O, pyr, CH_2Cl_2, 0 °C, 5 min (**12**; 75% in 2 steps).

*Synthesis of dicyclobutabenzene **9**:*

To a mixture of triflate **8** (8.82 g, 17.4 mmol) and ketene silyl acetal **4** (7.00 g, 34.6 mmol) in THF (115 mL) was added *n*-BuLi (1.63 M in hexane, 21 mL, 34 mmol) at –78 °C. After 5 min, the reaction mixture was poured into sat. aq. $NaHCO_3$. The products were extracted with EtOAc (X3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 9/1) to afford dicyclobutabenzene **9** (5.26 g, 69.6%) as a colorless oil.



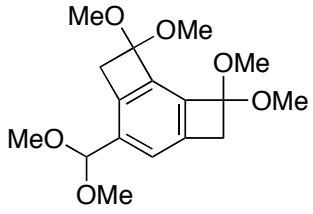
dicyclobutabenzene **9**

^{1}H NMR (acetone-d_6, δ)

0.13 (s, 3H), 0.14 (s, 3H), 0.90 (s, 9H), 1.14 (t, 3H, J = 7.1 Hz), 3.37 (d, 1H, J = 13.4 Hz), 3.42 (d, 1H, J = 13.4 Hz), 3.55 (s, 2H), 3.67 (qd, 1H, J_1 = 7.1, J_2 = 8.8 Hz), 3.86 (qd, 1H, J_1 = 7.1, J_2 = 8.8

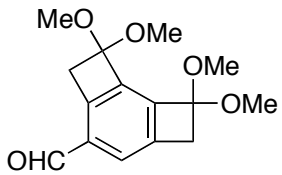
Hz), 3.92–4.21 (m, 8H), 5.74 (s, 1H), 7.22 (s, 1H);
^{13}C NMR (acetone-d_6, δ)
–3.6, –3.3, 15.5, 18.5, 26.0, 47.3, 49.2, 60.8, 65.6, 65.9, 102.8, 103.3, 110.2, 123.6, 136.2, 140.4, 141.1, 141.7, 141.9;
IR (neat)
2932, 2886, 1472, 1463, 1423, 1391, 1352, 1216, 1098, 1058, 964, 883, 840, 781 cm^{-1};
Anal. Calcd for $C_{23}H_{34}O_6Si$: C, 63.56; H, 7.89. Found: C, 63.61; H, 7.67.

*Synthesis of tris-dimethylacetal **iii**:*
To a solution of dicyclobutabenzene **9** (2.19 g, 5.04 mmol) in MeOH (20 mL) was added trimethylorthoformate (6.0 mL), followed by TsOH (100 mg, 0.53 mmol) at room temperature. After 10 h, the reaction mixture was poured into sat. aq. $NaHCO_3$. The products were extracted with EtOAc (X5) and combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 9/1) to afford tris-dimethylacetal **iii** (1.52 g, 93.0%) as a colorless oil.



tris-dimethylacetal **iii**
^{1}H NMR (acetone-d_6, δ)
3.26 (s, 6H), 3.29 (s, 2H), 3.32 (s, 2H), 3.40 (s, 12H), 5.39 (s, 1H), 7.21 (s, 1H);
^{13}C NMR (acetone-d_6, δ)
43.8, 44.4, 51.3, 52.6, 102.5, 106.3, 123.4, 136.6, 138.2, 138.4, 140.0, 141.6;
IR (neat)
2938, 2831, 1464, 1418, 1386, 1338, 1247, 1206, 1151, 1103, 1053, 984, 963, 847, 829 cm^{-1};
Anal. Calcd for $C_{17}H_{24}O_6$: C, 62.95; H, 7.46. Found: C, 62.74; H, 7.74.

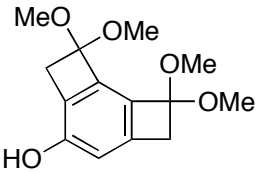
*Synthesis of aldehyde **10**:*
To a solution of tris-dimethylacetal **iii** (527 mg, 1.63 mmol) in THF (5.4 mL) was added 0.12 M H_2SO_4 (0.27 mL) at 0 °C. After warmed up to room temperature, and further stirred for 5 h, the reaction mixture was quenched with sat. $NaHCO_3$. The products were extracted with EtOAc (X3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/acetone = 9/1) to afford aldehyde **10** (439 mg, 96.7%) as a colorless oil.



aldehyde **10**
^{1}H NMR (acetone-d_6, δ)

3.38 (s, 2H), 3.42 (s, 6H), 3.43 (s, 6H), 3.57 (s, 2H), 7.69 (s, 1H), 10.0 (s, 1H);
^{13}C NMR (acetone-d_6, δ)
43.9, 44.4, 51.4, 51.5, 106.1, 106.6, 125.9, 134.2, 139.7, 142.9, 143.4, 144.7, 191.2;
IR (neat)
2939, 2833, 1697, 1261, 1248, 1205, 1140, 1118, 1069, 1054, 1032, 841 cm^{-1};
Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.98; H, 6.72.

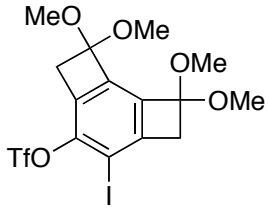
*Synthesis of phenol **11**:*
To a suspension of mCPBA (945 mg, 3.83 mmol) in CH_2Cl_2 (16 mL) was added aldehyde **10** (435 mg, 1.56 mmol) in CH_2Cl_2 (23 mL). After warmed up to 40 °C, and further stirred for 14 h, the reaction was quenched with sat. aq. $NaHCO_3$. The products were extracted with EtOAc (X3), and the combined organic extracts were washed successively with 10% aq. $Na_2S_2O_3$, sat. aq. $NaHCO_3$, and brine, and dried over Na_2SO_4. Evaporation of the solvents gave the crude product **iv**.
To a solution of the crude product **iv** in dioxane (16 mL) was added 0.1 M NaOH (16 mL) at 0 °C. After warm up to room temperature, and further stirred for 42 h, the reaction was stopped by adding water. The products were extracted with EtOAc (X3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (EtOAc/CH_2Cl_2 = 1/9) to afford phenol **11** (315 mg, 75.9%) as a colorless oil.



phenol **11**
^{1}H NMR (acetone-d_6, δ)
3.19 (s, 2H), 3.20 (s, 2H), 3.36 (s, 6H), 3.38 (s, 6H), 6.64 (s, 1H), 8.63 (s, 1H);
^{13}C NMR (acetone-d_6, δ)
41.8, 43.6, 51.2, 105.65, 105.74, 112.1, 125.6, 130.0, 140.2, 143.4, 154.9;
IR (neat)
3330, 2832, 1605, 1438, 1378, 1284, 1250, 1217, 1135, 1106, 1070, 1050, 1031, 963, 925, 857, 838, 797 cm^{-1};
Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.06; H, 6.72.

*Synthesis of iodo-triflate **12**:*
To a solution of phenol **11** (221 mg, 0.830 mmol) in CH_2Cl_2 (5 mL) was added diisopropylethylamine (0.5 mL), followed by $BnMe_3N^+ICl_2^-$ (303 mg, 0.871 mmol) in CH_2Cl_2 (5 mL) at –78 °C. After warm up to –50 °C, and further stirred for 6.5 h, the reaction was stopped by adding sat. aq. NH_4Cl. The products were extracted with EtOAc (X3), and the combined organic extracts were washed with 10% aq. $Na_2S_2O_3$, and brine, dried over Na_2SO_4. Evaporation of the solvents gave crude iodo-phenol **v**.
To a solution of iodo-phenol **v** in CH_2Cl_2–pyridine (4 mL/1 mL) was slowly added Tf_2O (257 mg, 0.911 mmol) in CH_2Cl_2 (4 mL) at 0 °C. After 5 min, the reaction mixture was poured into sat. $NaHCO_3$. The products were extracted with EtOAc (X3), and the combined organic extracts

were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 95/5) to give iodo-triflate **12** (326 mg, 74.9%) as a colorless oil.



iodo-triflate **12**

^{1}H NMR (acetone-d_6, δ)

3.23 (s, 2H), 3.43 (s, 6H), 3.43 (s, 6H), 3.51 (s, 2H);

^{13}C NMR (acetone-d_6, δ)

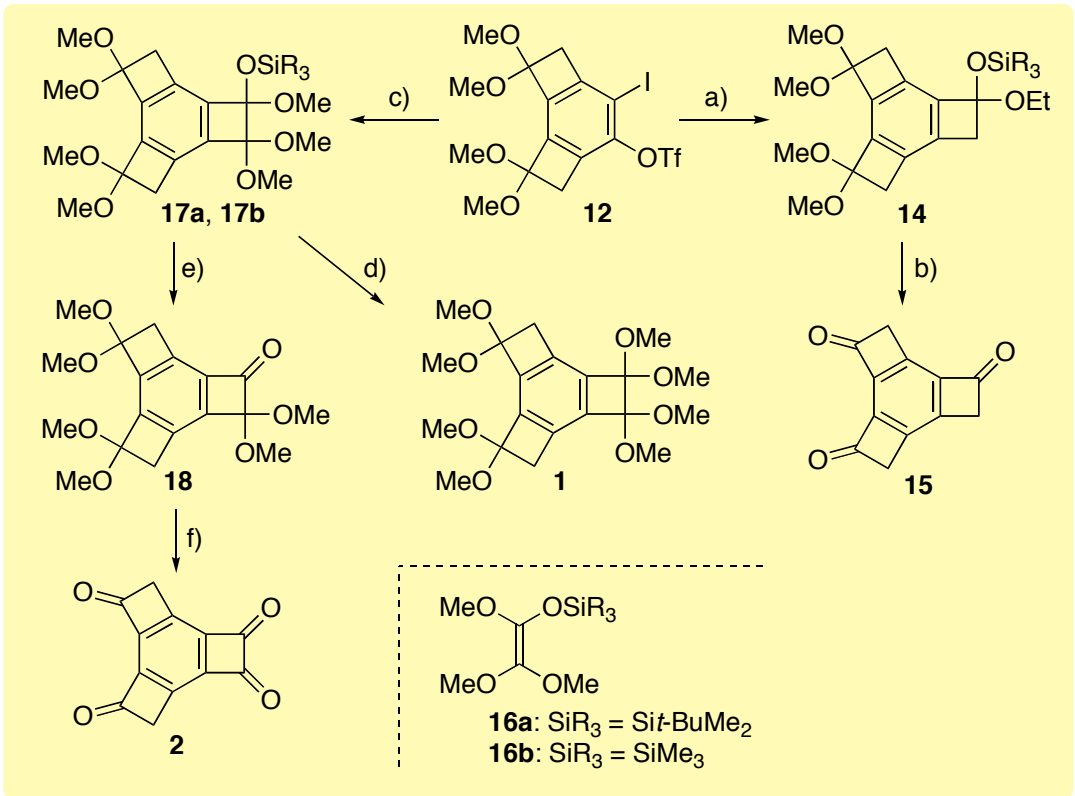
44.0, 46.7, 51.5, 51.6, 86.3, 102.7, 104.8, 119.4 (q, J_{C-F} = 320 Hz), 133.8, 138.3, 141.4, 145.8, 151.8;

IR (neat)

2943, 2835, 1611, 1427, 1366, 1237, 1214, 1141, 1068, 1050, 1031, 1012, 964, 929, 852, 790, 763 cm^{-1};

Anal. Calcd for $C_{15}H_{16}O_7F_3IS$: C, 34.37; H, 3.08; S, 6.12. Found: C, 34.41; H, 3.28, S, 6.33.

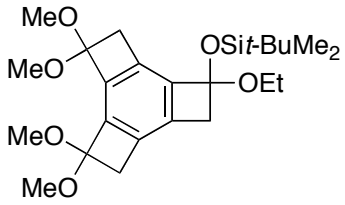
Scheme 3. Third [2+2] cycloaddition



Reagents and conditions: a) **4**, *n*-BuLi, THF, –78 °C, 5 min (**14**: 79%); b) aq. HF, CH_3CN, –10 °C → r.t., 2 h (**15**: 92%); c) **16a** or **16b**, *n*-BuLi, Et_2O, –78 °C, 5 min; d) TsOH, MeOH, r.t., 50 h (**1**: 55%, in 2 steps); e) aq. HF, CH_3CN, –16 °C, 20 min (**18**: 58%, in 2 steps); f) BF_3•Et_2O, H_2O, THF, –20 °C → r.t., 2 h (**2**: 84%).

*Synthesis of tricyclobutabenzene **14**:*

To a mixture of triflate **12** (197 mg, 0.376 mmol) and ketene silyl acetal **4** (381 mg, 1.88 mmol) in THF (8.5 mL) was added *n*-BuLi (1.58 M in hexane, 0.39 mL, 0.62 mmol) at –78 °C. After 5 min, the reaction was stopped by adding water. The products were extracted with EtOAc (X3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 95/5) to afford **14** (134 mg, 79.3%) as a colorless oil.



tricyclobutabenzen **14**

^{1}H NMR (acetone-d_6, δ)

0.09 (s, 3H), 0.13 (s, 3H), 0.89 (s, 9H), 1.15 (t, 3H, J = 7.1 Hz), 3.27–3.41 (m, 18H), 3.59 (qd, 1H, J_1 = 7.1, J_2 = 9.0 Hz), 3.82 (qd, 1H, J_1 = 7.1, J_2 = 9.0 Hz);

^{13}C NMR (acetone-d_6, δ)

–3.5, –3.4, 15.6, 18.5, 26.0, 43.3, 44.3, 48.7, 51.28, 51.301, 51.306, 51.318, 61.2, 104.1, 106.8, 107.1, 133.9, 136.3, 138.3, 138.5, 140.3, 145.7;

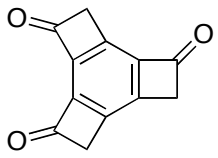
IR (neat)

2956, 2932, 2857, 2832, 1260, 1227, 1181, 1138, 1052, 1032, 939, 851, 839, 780 cm^{-1};

Anal. Calcd for $C_{24}H_{38}O_6Si$: C, 63.97; H, 8.50. Found: C, 63.99; H, 8.66.

*Synthesis of triketone **15**:*

To a solution of tricyclobutabenzene **14** (51.9 mg, 0.115 mmol) in CH_3CN (1.5 mL) was added 46% aq. HF (0.1 mL) at –10 °C. After warm up to room temperature, and further stirred for 2 h, the reaction was stopped by adding water. The products were extracted with EtOAc (X3) and the combined organic extracts were washed with sat. aq. $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/acetone = 6/4) to afford triketone **15** (20.9 mg, 91.7%). Recrystallization from hexane-EtOAc gave **15** as colorless needles. Mp 136.2–136.8 °C.



triketone **15**

^{1}H NMR ($CDCl_3$, δ)

4.16 (s, 2H), 4.21 (s, 2H), 4.24 (s, 2H);

^{13}C NMR ($CDCl_3$, δ)

53.2, 53.5, 54.1, 143.0, 145.7, 146.7, 147.4, 148.4, 152.3, 182.6, 183.5, 185.2;

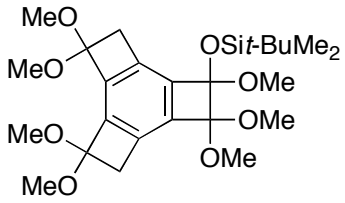
IR (KBr)

2983, 2935, 2852, 1788, 1770, 1583, 1408, 1356, 1221, 1173, 1086, 968, 941, 808 cm^{-1};

Anal. Calcd for $C_{12}H_6O_3$: C, 72.73; H, 3.05. Found: C, 72.43; H, 3.24.

*Synthesis of tricyclobutabenzene **17a**:*

To a mixture of triflate **12** (83.2 mg, 0.159 mmol) and ketene silyl acetal **16a** (99.1 mg, 0.399 mmol) in Et_2O (1.5 mL) was added *n*-BuLi (1.58 M in hexane, 0.15 mL, 0.24 mmol) at –78 °C. After 5 min, the reaction mixture was poured into water. The products were extracted with EtOAc (X3) and the combined organic extracts were washed brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 8/2) to afford tricyclobutabenzene **17a** (48.3 mg, 61.1%) as a colorless oil.



tricyclobutabenzene **17a**

^{1}H NMR (acetone-d_6, δ)

0.021 (s, 3H), 0.024 (s, 3H), 0.92 (s, 9H), 3.37–3.43 (m, 25H);

^{13}C NMR (acetone-d_6, δ)

–3.6, –3.4, 19.0, 26.2, 44.2, 44.7, 51.37, 51.38, 51.43, 51.5, 51.7, 52.2, 52.8, 106.7, 106.8, 108.7, 111.3, 135.4, 135.9, 140.8, 141.1, 141.4, 144.2;

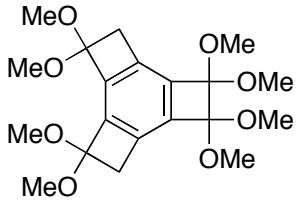
IR (neat)

2935, 2856, 2832, 1463, 1380, 1250, 1226, 1140, 1078, 1054, 1032, 850, 780 cm^{-1};

Anal. Calcd for $C_{25}H_{40}O_8Si$: C, 60.46; H, 8.12. Found: C, 60.43; H, 8.16.

*Synthesis of tetra-dimethylacetal **1**:*

To a solution of tricyclobutabenzene **17a** (36.2 mg, 0.0729 mmol) in MeOH (1.0 mL) was added trimethylorthoformate (0.2 mL), followed by TsOH (2.8 mg, 0.0146 mmol) at room temperature. After 50 h, the reaction mixture was poured into sat. aq. $NaHCO_3$. The products were extracted with EtOAc (X3) and combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/acetone = 7/3) to afford tetra-dimethylacetal **1** (26.0 mg, 90.0%). Recrystallization from hexane–EtOAc gave **1** as colorless prisms. Mp 172.0 –172.8 °C.



tricyclobutabenzene **1**

^{1}H NMR (acetone-d_6, δ)

3.42 (s, 4H), 3.43 (s, 12H), 3.47 (s, 12H);

^{13}C NMR (acetone-d_6, δ)

43.6, 51.3, 52.3, 106.0, 110.4, 135.2, 140.1, 140.3;

IR (KBr)

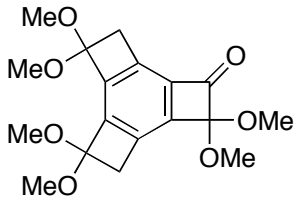
2991, 2941, 2908, 2831, 1618, 1458, 1383, 1273, 1225, 1142, 1082, 1030, 982, 849 cm^{-1};

Anal. Calcd for $C_{20}H_{28}O_8$: C, 60.59; H, 7.12. Found: C, 60.36; H, 6.89.

*Synthesis of tricyclobutabenzene **18**:*

To a mixture of triflate **12** (58.4 mg, 0.111 mmol) and ketene silyl acetal **16b** (53.7 mg, 0.260 mmol) in Et_2O (3.0 mL) was added *n*-BuLi (1.58 M in hexane, 0.15 mL, 0.24 mmol) at –78 °C. After 5 min, the reaction was stopped by adding water. Extractive workup (EtOAc) followed by evaporation gave crude cycloadduct **17b**.

To a solution of the crude product **17b** in CH_3CN (1.5 mL) was added 46% aq. HF (0.1 mL) at –16 °C. After 20 min, the mixture was diluted by water, and the products were extracted with EtOAc (X3), washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 7/3) to afford **18** (22.6 mg, 58.1%) as a pale yellow oil.



tricyclobutabenzene **18**

^{1}H NMR (acetone-d_6, δ)

3.44 (s, 6H), 3.45 (s, 6H), 3.48 (s, 2H), 3.49 (s, 6H), 3.56 (s, 2H);

^{13}C NMR (acetone-d_6, δ)

44.1, 44.8, 51.62, 51.59, 52.9, 106.7, 107.1, 118.0, 136.5, 138.4, 143.2, 145.2, 145.5, 155.6, 188.9;

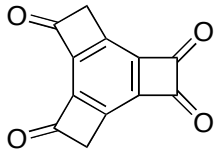
IR (neat)

2995, 2941, 2912, 2835, 1774, 1234, 1171, 1136, 1076, 1053, 1016, 850 cm^{-1};

Anal. Calcd for $C_{18}H_{22}O_7$: C, 61.71; H, 6.33. Found: C, 61.65; H, 6.58.

*Synthesis of tetraketone **2**:*

To a solution of BF_3•OEt_2 (104 mg, 0.733 mmol) in CH_2Cl_2 (1.5 mL) was added tricyclobutabenzene **18** (16.1 mg, 0.046 mmol) in CH_2Cl_2 (2.5 mL) and H_2O (15 μL) at –20 °C. After warm up to room temperature, and further stirred for 2 h, the reaction was stopped by adding silica-gel. The mixture was filtered through cotton plug by washing EtOAc, and the filtrate were concentrated in vacuo. The residue was washed by Et_2O to afford essentially pure tetraketone **2** (8.2 mg, 84%). Recrystallization from hexane–EtOAc at –10 °C gave **2** as yellow prisms. Mp > 300 °C (decomposed).



tetraketone **2**

^{1}H NMR (acetone-d_6, δ)

4.50 (s, 4H);

^{13}C NMR (acetone-d_6, δ)

55.3, 145.6, 149.1, 172.6, 183.7, 193.1;

IR (KBr)

2985, 2929, 2850, 1772, 1408, 1367, 1313, 1257, 1219, 1176, 1074, 1053, 982, 870, 795, 748, 708 cm^{-1};

Anal. Calcd for $C_{12}H_4O_4$: C, 67.93; H, 1.90. Found: C, 67.68; H, 2.17.