Supporting Information

Siloxyl(trialkoxy)ethene Undergoes Regioselective [2+2] Cycloaddition to Yrones and Ynoates en route to Functionalized Cyclobutenediones

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General Experimental Procedures

All experiments dealing with air- and moisture-sensitive compounds were conducted under an atmosphere of dry argon.

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. ¹H NMR and ¹³C NMR were measured on a JEOL JNM lambda-400, a JEOL JNM ECA-400, and a Bruker AV400N spectrometer. Infrared (IR) spectra were recorded on a Jasco IR-Report-100, and a Horiba FT-710 spectrometer. Attenuated Total Reflectance Fourier Transformation Infrared (ATR-FTIR) spectra were recorded on a Perkin Elmer 1600 FTIR. Elementary analyses were performed by using Perkin Elmer series II 2004.
**Synthesis of cyclobutene 3:**
A mixture of 3-butyne-2-one (1) (131 mg, 1.92 mmol) and KSA 2 (627 mg, 2.52 mmol) was heated at 60 °C for 8 h. The crude product was purified by silica-gel flash column chromatography (hexane/EtOAc = 9/1) to give 3 (564 mg, 92.6%) as a colorless oil.

![Cyclobutene 3](image)

**cyclobutene 3**

$^1$H NMR (acetone-$d_6$, $\delta$)
- 0.08 (s, 3H), 0.14 (s, 3H), 0.90 (s, 9H), 2.29 (s, 3H), 3.33 (s, 3H), 3.36 (s, 3H), 3.39 (s, 3H), 7.33 (s, 1H);

$^{13}$C NMR (acetone-$d_6$, $\delta$)

IR (neat)
- 2937, 2856, 1689, 1606, 1463, 1361, 1276, 1251, 1195, 1095, 1014, 998, 898, 838, 781 cm$^{-1}$;

Anal. Calcd for C$_{15}$H$_{28}$O$_5$Si: C, 56.93; H, 8.92. Found: C, 56.77; H, 9.01.

![1,3-Diene 4](image)

**1,3-diene 4**

$^1$H NMR (acetone-$d_6$, $\delta$)
- 0.15 (s, 6H), 0.91 (s, 9H), 1.86 (s, 3H), 3.49 (s, 3H), 3.60 (s, 3H), 3.63 (s, 3H), 4.30 (s, 1H);

$^{13}$C NMR (acetone-$d_6$, $\delta$)
- $-3.7, 18.6, 20.0, 26.0, 51.1, 55.6, 56.1, 76.3, 111.8, 148.8, 159.7, 169.3$;

IR (neat)
- 2950, 2897, 2858, 1734, 1667, 1619, 1462, 1434, 1381, 1324, 1254, 1213, 1169, 1104, 1076, 1002, 939, 863, 838, 813, 780 cm$^{-1}$.

*The stereochemistry of 4 was determined on the basis of the observed NOE shown below.*

![NOE](image)
**Scheme 1.** Determination of the regiochemistry

\[
\begin{aligned}
&\text{OSi} \cdot \text{BuMe}_2 \quad \text{OMe} \quad \text{OMe} \\
&\text{Me} \quad \text{HO} \\
&\text{NaBH}_4, \text{CeCl}_3 \cdot 7\text{H}_2\text{O} \\
&\text{MeOH, 0 °C} \\
&\text{99%} \\
\end{aligned}
\]

**Synthesis of alcohol i:**

To a solution of cyclobutene 3 (33.5 mg, 0.106 mmol) in MeOH (0.3 mL) was added CeCl$_3 \cdot 7$H$_2$O (43.5 mg, 0.117 mmol) and NaBH$_4$ (4.5 mg, 0.119 mmol) at 0 °C. After 1 h, the reaction was stopped by adding water. The products were extracted with Et$_2$O (X3), and the combined organic extracts were washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuo. The residue was purified by PTLC (hexane/CH$_2$Cl$_2$/Et$_2$O = 50/25/25) to give alcohol i (33.3 mg, 98.8%) as a mixture of diasteromers. Recrystallization from hexane gave ia as colorless prisms. Mp 72.0–73.5 °C.

**alcohol ia**

$^1$H NMR (acetone-$d_6$, δ)

0.149 (s, 3H), 0.154 (s, 3H), 0.90 (s, 9H), 1.32 (d, 3H, $J = 6.8$ Hz), 3.27 (s, 3H), 3.30 (s, 3H), 3.41 (s, 3H), 3.89 (d, 1H, $J = 5.3$ Hz), 4.40–4.50 (m, 1H), 6.47 (d, 1H, $J = 1.4$ Hz);

$^{13}$C NMR (acetone-$d_6$, δ)

−2.9, −2.7, 19.0, 22.8, 26.5, 50.87, 50.91, 53.2, 64.2, 107.7, 108.3, 131.4, 161.6;

IR (ATR)

3501, 2938, 2893, 2857, 1467, 1436, 1387, 1359, 1333, 1277, 1243, 1193, 1165, 1080, 1058, 1009, 982, 905, 829, 780, 727 cm$^{-1}$;

Anal. Calcd for C$_{15}$H$_{30}$O$_5$Si: C, 56.57; H, 9.49. Found: C, 56.65; H, 9.42.

$^2$ The stereochemistry of alcohol ia was determined by X-ray analysis shown below.$^{[1]}$

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$^{[1]}$ CCDC-662792 (ia) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
alcohol ib

$^1$H NMR (acetone-$d_6$, δ)
0.14 (s, 3H), 0.14 (s, 3H), 0.89 (s, 9H), 1.29 (d, 3H, J = 6.6 Hz), 3.26 (s, 3H), 3.30 (s, 3H), 3.40 (s, 3H), 3.95 (d, 1H, J = 5.1 Hz), 4.40–4.50 (m, 1H), 6.44 (d, 1H, J = 1.4 Hz);

$^{13}$C NMR (acetone-$d_6$, δ)
−3.2, −2.9, 19.1, 23.0, 26.3, 51.0, 51.2, 52.3, 63.9, 106.9, 109.0, 130.7, 161.7;

IR (neat)
3454, 2952, 2935, 2856, 2832, 1473, 1463, 1438, 1373, 1361, 1276, 1253, 1193, 1164, 1089, 1058, 1018, 989, 921, 894, 836, 779, 730 cm$^{-1}$


Synthesis of cyclobutene 6a:

According to the general procedure for synthesis of cyclobutene 3, ynone 5a$^{[2]}$ (124 mg, 0.953 mmol) and KSA 2 (318 mg, 1.28 mmol) gave, after purification by silica-gel flash column chromatography (hexane/EtOAc = 9/1), 6a (337 mg, 93.4%) as a yellow oil.

$^1$H NMR (acetone-$d_6$, δ)
0.08 (s, 3H), 0.16 (s, 3H), 0.89 (s, 9H), 3.39 (s, 3H), 3.42 (s, 3H), 3.47 (s, 3H), 7.21 (s, 1H), 7.52–7.60 (m, 2H), 7.64–7.70 (m, 1H), 7.93–7.98 (m, 2H);

$^{13}$C NMR (acetone-$d_6$, δ)

–3.2, –3.1, 19.0, 26.3, 51.3, 51.4, 53.4, 108.2, 108.9, 129.6, 129.8, 134.2, 137.9, 145.3, 151.3, 190.4;
IR (neat)
3066, 2937, 2904, 2856, 2835, 1660, 1598, 1580, 1472, 1463, 1448, 1360, 1318, 1278, 1256, 1193, 1150, 1107, 1090, 1065, 1013, 941, 892, 874, 839, 801, 781, 721 cm⁻¹;
Anal. Calcd for C₂₀H₃₀O₅Si: C, 63.46; H, 7.99. Found: C, 63.34; H, 8.00.

Synthesis of cyclobutene 6b:
According to the general procedure for synthesis of cyclobutene 3, ynone 5b[2] (78.3 mg, 0.501 mmol) and KSA₂ (178 mg, 0.717 mmol) gave, after purification by silica-gel flash column chromatography (hexane/EtOAc = 9/1), 6b (180 mg, 88.8%). Recrystallization from hexane gave 6b as yellow prisms. Mp. 68.0–69.2 °C.

1H NMR (acetone-d₆, δ)
0.13 (s, 3H), 0.18 (s, 3H), 0.93 (s, 9H), 3.38 (s, 3H), 3.41 (s, 3H), 3.48 (s, 3H), 7.41 (d, 1H, J = 15.8 Hz), 7.45–7.50 (m, 3H), 7.54 (s, 1H), 7.71 (d, 1H, J = 15.8 Hz), 7.75–7.82 (m, 2H);
13C NMR (acetone-d₆, δ)
–3.2, –3.1, 19.1, 26.4, 51.3, 51.4, 53.3, 107.2, 108.6, 124.0, 129.5, 129.8, 131.6, 135.6, 144.3, 145.3, 153.2, 186.2;
IR (ATR)
3062, 3026, 2937, 2903, 2856, 2834, 1666, 1636, 1597, 1576, 1495, 1473, 1462, 1450, 1408, 1388, 1339, 1277, 1180, 1093, 1066, 1010, 999, 912, 887, 838, 796, 781, 766, 727 cm⁻¹;

Synthesis of cyclobutene 6c:
According to the general procedure for synthesis of cyclobutene 3, ynone 5c[3] (53.5 mg, 0.399 mmol) and KSA₂ (141 mg, 0.568 mmol) gave, after purification by PTLC (hexane/EtOAc = 7/3), 6c (115 mg, 75.4%) as a colorless oil.

1H NMR (acetone-d₆, δ)
0.05 (s, 3H), 0.13 (s, 3H), 0.89 (s, 9H), 1.58–1.70 (m, 4H), 2.16–2.36 (m, 4H), 3.34 (s, 3H), 3.36 (s, 3H), 3.43 (s, 3H), 6.93 (s, 1H), 7.08–7.12 (m, 1H);
13C NMR (acetone-d₆, δ)
–3.14, –3.11, 18.9, 22.3, 22.5, 23.5, 26.3, 26.7, 51.16, 51.23, 53.4, 108.5, 108.7, 139.9, 141.8, 145.3, 152.0, 191.4;

IR (neat)
3068, 2935, 2857, 2834, 1647, 1637, 1472, 1460, 1437, 1388, 1378, 1343, 1306, 1278, 1248, 1192, 1139, 1099, 1064, 1013, 971, 927, 889, 838, 799, 781, 749, 706 cm⁻¹; 
Anal. Calcd for C₂₀H₃₄O₅Si: C, 62.79; H, 8.96. Found: C, 63.02; H, 8.75.

Synthesis of cyclobutene 6d:
According to the general procedure for synthesis of cyclobutene 3, ynone 5d\(^4\) (148 mg, 0.960 mmol) and KSA 2 (323 mg, 1.30 mmol) gave, after purification by silica-gel flash column chromatography (hexane/EtOAc = 19/1), 6d (377 mg, 97.6%) as a colorless oil.

\[
\begin{align*}
\text{Ph} & \quad \text{O} & \quad \text{Si}^{t} & \quad \text{BuMe}_2 \\
\text{OMe} & \quad \text{OMe} & \quad \text{OMe} & \quad \text{OMe}
\end{align*}
\]

Cyclobutene 6d

\(^1\)H NMR (acetone-\(d_6\), δ)
0.13 (s, 3H), 0.17 (s, 3H), 0.91 (s, 9H), 3.38 (s, 3H), 3.41 (s, 3H), 3.45 (s, 3H), 7.45–7.65 (m, 3H), 7.69 (s, 1H), 7.72–7.80 (m, 2H);

\(^1^3\)C NMR (acetone-\(d_6\), δ)
−3.4, −3.3, 19.1, 26.2, 51.3, 51.5, 53.4, 86.9, 92.8, 106.6, 108.1, 120.3, 129.8, 132.2, 134.1, 149.9, 152.8, 173.3;

IR (neat)
3065, 2938, 2856, 2836, 2200, 1644, 1597, 1490, 1471, 1463, 1443, 1318, 1273, 1190, 1093, 1099, 896, 838, 798, 781, 758, 688 cm⁻¹;

Synthesis of cyclobutene 6e:
According to the general procedure for synthesis of cyclobutene 3, ynoate 5e\(^5\) (40.0 mg, 0.273 mmol) and KSA 2 (89.5 mg, 0.360 mmol) gave, after purification by PTLC (hexane/EtOAc = 9/1), 6e (101 mg, 93.5%) as a colorless oil.

\[
\begin{align*}
\text{PhO} & \quad \text{O} & \quad \text{Si}^{t} & \quad \text{BuMe}_2 \\
\text{OMe} & \quad \text{OMe} & \quad \text{OMe} & \quad \text{OMe}
\end{align*}
\]

Cyclobutene 6e

\(^1\)H NMR (acetone-\(d_6\), δ)
0.17 (s, 3H), 0.19 (s, 3H), 0.93 (s, 9H), 3.38 (s, 3H), 3.41 (s, 3H), 3.51 (s, 3H), 7.17–7.21 (m, 2H), 7.25–7.32 (m, 1H), 7.42–7.48 (m, 2H), 7.54 (s, 1H);

\(^1^3\)C NMR (acetone-\(d_6\), δ)
−3.3, −3.1, 19.0, 26.2, 51.3, 51.4, 53.0, 106.9, 108.6, 122.4, 126.9, 130.4, 145.8, 149.1, 151.2, 160.5;
IR (neat)

Synthesis of cyclobutene 8a:
To a solution of ynoate 7a\(^5\) (80.1 mg, 0.488 mmol) in toluene (1.0 mL) was added Me\(_3\)Al (1.03 M in hexane, 0.48 mL, 0.49 mmol) and KSA 2 (141 mg, 0.567 mmol) in toluene (1.0 mL) at –78 °C. After warmed up to –20 °C and further stirred for further 69 h, the reaction was stopped by adding sat. aq. NaHCO\(_3\). The products were extracted with EtOAc and combined organic extracts were washed with brine, dried (Na\(_2\)SO\(_4\)), and concentrated in vacuo. The residue was purified by PTLC (hexane/CH\(_2\)Cl\(_2\)/Et\(_2\)O = 70/15/15) to give cyclobutene 8a (89.4 mg, 44.4%) and adduct 9a (57.5 mg, 28.6%).

\[
\text{MeO}_2\text{C} \quad \text{OMe} \quad \text{OSi-t-BuMe}_2 \quad \text{OMe} \quad \text{OMe}
\]

cyclobutene 8a (colorless oil)
\(^1^H\) NMR (acetone-\(d_6\), \(\delta\))
0.10 (s, 3H), 0.14 (s, 3H), 0.91 (s, 9H), 1.55–1.67 (m, 4H), 2.14–2.43 (m, 4H), 3.40 (s, 3H), 3.41 (s, 3H), 3.42 (s, 3H), 3.73 (s, 3H), 6.58–6.61 (m, 1H);
\(^1^3\)C NMR (acetone-\(d_6\), \(\delta\))
–3.1, –3.0, 19.0, 22.2, 23.0, 26.3, 26.5, 26.9, 51.4, 52.4, 52.5, 52.6, 106.7, 109.2, 132.8, 133.5, 137.5, 156.8, 163.6;
IR (neat)
2936, 2857, 1720, 1627, 1461, 1434, 1268, 1245, 1218, 1199, 1087, 1025, 998, 952, 890, 836, 802, 779, 728 cm\(^{-1}\);

\[
\text{MeO}_2\text{C} \quad \text{O} \quad \text{Si-t-BuMe}_2 \quad \text{OMe} \quad \text{OMe} \quad \text{OMe}
\]

adduct 9a (colorless oil)
\(^1^H\) NMR (acetone-\(d_6\), \(\delta\))
0.205 (s, 3H), 0.211 (s, 3H), 0.90 (s, 9H), 1.56–1.67 (m, 4H), 2.10–2.12 (m, 4H), 3.381 (s, 3H), 3.383 (s, 3H), 3.40 (s, 3H), 3.65 (s, 3H), 6.10–6.18 (m, 1H);
\(^1^3\)C NMR (acetone-\(d_6\), \(\delta\))
–3.4, –2.6, 18.8, 22.0, 22.8, 26.08, 26.13, 29.3, 51.85, 51.92, 52.01, 52.02, 84.2, 90.1, 97.3, 104.3, 120.6, 136.5, 167.5;
IR (neat)
2935, 2857, 2217, 1751, 1461, 1434, 1388, 1361, 1284, 1249, 1214, 1126, 1072, 1018, 960, 937, 879, 840, 782, 717 cm\(^{-1}\);
Synthesis of cyclobutene 8b:
According to the general procedure for synthesis of 8a, ynoate 7b[5] (90.1 mg, 0.506 mmol), KSA 2 (147 mg, 0.592 mmol), and Me3Al (1.03 M in hexane, 0.50 mL, 0.51 mmol) gave, after purification by PTLC (hexane/EtOAc = 9/1), cyclobutene 8b (105 mg, 48.7%) and adduct 9b (61.8 mg, 28.7%).

Synthesis of cyclobutene 8c:
According to the general procedure for synthesis of cyclobutene 8a, ynoate 7c (47.0 mg, 0.244 mmol), KSA 2 (72.0 mg, 0.290 mmol), and Me3Al (1.02 M in hexane, 0.24 mL, 0.24 mmol) gave, after purification by PTLC (hexane/EtOAc = 9/1), cyclobutene 8c (63.9 mg, 59.3%) and adduct 9c (10.8 mg, 10.0%).
cyclobutene 8c (colorless oil)

$^1$H NMR (acetone-$d_6$, $\delta$)

0.14 (s, 3H), 0.16 (s, 3H), 0.91 (s, 9H), 1.27 (d, 3H, $J = 6.4$ Hz), 1.28 (d, 3H, $J = 6.4$ Hz), 1.54–1.70 (m, 4H), 2.15–2.22 (m, 2H), 2.28–2.37 (m, 2H), 3.397 (s, 3H), 3.401 (s, 3H), 3.43 (s, 3H), 5.08 (sept, 1H, $J = 6.4$ Hz), 6.54–6.57 (m, 1H);

$^{13}$C NMR (acetone-$d_6$, $\delta$)

–2.9, –2.8, 19.0, 21.9, 22.0, 22.2, 23.0, 26.4, 26.4, 27.1 52.1 52.6, 52.9, 68.7, 106.9, 109.0, 131.9, 134.5, 136.7, 155.9, 163.0;

IR (neat)

2935, 2857, 2838, 1712, 1627, 1465, 1384, 1357, 1307, 1268, 1249, 1222, 1195, 1091, 1022, 998, 952, 921, 890, 836, 806, 779, 725 cm$^{-1}$;


adduct 9c (colorless oil)

$^1$H NMR (acetone-$d_6$, $\delta$)

0.23 (s, 3H), 0.24 (s, 3H), 0.90 (s, 9H), 1.16 (d, 6H, $J = 6.4$ Hz), 1.54–1.70 (m, 4H), 2.06–2.15 (m, 4H), 3.407 (s, 3H), 3.410 (s, 3H), 3.65 (s, 3H), 4.28 (sept, 1H, $J = 6.4$ Hz), 6.10–6.17 (m, 1H);

$^{13}$C NMR (acetone-$d_6$, $\delta$)

–3.1, –2.4, 18.8, 22.0, 22.7, 23.5, 24.7, 26.0, 26.2, 51.7 51.9, 52.3, 68.1, 85.6, 88.7, 96.6, 104.1, 120.7, 136.2, 167.8;

IR (neat)

2935, 2857, 2217, 1751, 1627, 1465, 1434, 1380, 1361, 1284, 1249, 1214, 1114, 1064, 1041, 956, 917, 887, 836, 802, 779, 717 cm$^{-1}$;


**Synthesis of cyclobutene 8d:**

According to the general procedure for synthesis of cyclobutene 8a, alkyne 7d (118 mg, 0.521 mmol), KSA 2 (167 mg, 0.672 mmol), and Me$_3$Al (1.03 M in hexane, 0.50 mL, 0.51 mmol) gave, after purification by PTLC (hexane/EtOAc = 8/2), 8d (182 mg, 73.5%) as a colorless oil.
3.455 (s, 3H), 3.459 (s, 3H), 3.53 (s, 3H), 6.68–6.72 (m, 1H), 7.14–7.32 (m, 3H), 7.42–7.48 (m, 2H);
$^{13}$C NMR (acetone-$d_6$, δ)
–3.0, –2.8, 19.0, 22.1, 23.0, 26.3, 26.6, 27.2, 52.3, 52.7, 53.0, 106.9, 109.2, 122.5, 126.8, 130.3, 132.1 132.7, 138.6, 151.3, 159.0, 161.6;
IR (KBr)
3062, 2935, 2857, 1731, 1619, 1592, 1492, 1249, 1191, 1164, 1087, 1018, 998, 952, 890, 836, 802, 779 cm$^{-1}$;
Anal. Calcd for C$_{26}$H$_{38}$O$_6$Si: C, 65.79; H, 8.07. Found: C, 65.58; H, 8.32.

**Synthesis of cyclobutene 11a:**
According to the general procedure for synthesis of cyclobutene 8a, ynoate 10a (103 mg, 0.509 mmol), KSA 2 (153 mg, 0.616 mmol), and Me$_3$Al (1.03 M in hexane, 0.50 mL, 0.51 mmol) gave, after purification by PTLC (hexane/CH$_2$Cl$_2$/Et$_2$O = 70/15/15), 11a (210 mg, 91.5%) as a colorless oil.

![Cyclobutene 11a structure]

$^1$H NMR (acetone-$d_6$, δ)
0.17 (s, 3H), 0.19 (s, 3H), 0.91 (t, 3H, J = 7.3 Hz), 0.93 (s, 9H), 1.36–1.48 (m, 2H), 1.65–1.76 (m, 2H), 2.68 (t, 2H, J = 7.0 Hz), 3.45 (s, 3H), 3.47 (s, 3H), 3.50 (s, 3H), 7.15–7.32 (m, 3H), 7.40–7.50 (m, 2H);
$^{13}$C NMR (acetone-$d_6$, δ)
IR (neat)
3064, 2958, 2937, 2857, 1737, 1656, 1592, 1492, 1463, 1288, 1247, 1191, 1074, 1024, 937, 838, 781, 736 cm$^{-1}$;
Anal. Calcd for C$_{24}$H$_{38}$O$_6$Si: C, 63.97; H, 8.50. Found: C, 63.73; H, 8.35.

![Key HMBC correlations table]

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Synthesis of cyclobutene 11b:
According to the general procedure for synthesis of cyclobutene 8a, ynoate 10b (1.09 g, 4.90 mmol), KSA 2 (1.48 g, 5.96 mmol), and Me₃Al (1.05 M in hexane, 4.6 mL, 4.8 mmol) gave, after purification by silica-gel flash column chromatography (hexane/EtOAc = 9/1), cyclobutene 11b (1.88 g, 81.4%) as a colorless oil.

\[
\text{PhO}_2\text{C}\quad \text{OSi-t-BuMe}_{2}\quad \text{OMe} \\
\text{OMe} \\
\text{OMe}
\]

cyclobutene 11b

$^1$H NMR (acetone-$d_6$, δ)
0.19 (s, 3H), 0.24 (s, 3H), 0.96 (s, 9H), 3.43 (s, 3H), 3.44 (s, 3H), 3.61 (s, 3H), 7.18–7.33 (m, 3H), 7.21–7.51 (m, 5H), 8.04–8.16 (m, 2H);

$^{13}$C NMR (acetone-$d_6$, δ)
–2.9, –2.7, 19.0, 26.3, 52.4, 52.6, 53.2, 107.0, 109.4, 122.5, 126.9, 129.1, 130.4, 130.6, 131.6, 132.0, 135.2, 151.1, 158.7, 161.4;

IR (neat)
3068, 2938, 2856, 1731, 1631, 1590, 1490, 1276, 1193, 1087, 1022, 995, 894, 836, 781 cm$^{-1}$;

Anal. Calcd for C$_{26}$H$_{34}$O$_6$Si: C, 66.35; H, 7.28. Found: C, 66.12; H, 7.47.

Synthesis of cyclobutene 11c:
According to the general procedure for synthesis of cyclobutene 8a, ynoate 10c (127 mg, 0.475 mmol), KSA 2 (151 mg, 0.608 mmol), and Me$_3$Al (1.03 M in hexane, 0.50 mL, 0.52 mmol) gave, after purification by PTLC (hexane/EtOAc = 7/3), cyclobutene 11c (209 mg, 85.3%) as a colorless oil.

\[
\text{PhO}_2\text{C}\quad \text{OSi-t-BuMe}_{2}\quad \text{OMe} \\
\text{OMe} \\
\text{Br}
\]

cyclobutene 11c

$^1$H NMR (acetone-$d_6$, δ)
0.16 (s, 3H), 0.19 (s, 3H), 0.92 (s, 9H), 2.18–2.30 (m, 2H), 2.80–2.92 (m, 2H), 3.37 (t, 2H, J = 7.0 Hz), 3.46 (s, 3H), 3.48 (s, 3H), 3.49 (s, 3H), 7.18–7.24 (m, 2H), 7.26–7.34 (m, 1H), 7.42–7.50 (m, 2H);

$^{13}$C NMR (acetone-$d_6$, δ)
–3.2, –3.0, 6.9, 19.0, 26.3, 29.7, 32.0, 51.7, 51.9, 52.9, 106.3, 108.7, 122.5, 126.8, 130.3, 138.5, 151.1, 161.1, 165.2;

IR (neat)
2937, 2903, 2856, 2835, 1738, 1657, 1592, 1492, 1472, 1462, 1388, 1359, 1283, 1247, 1192, 1162, 1109, 1078, 1041, 1024, 943, 9142 838, 780, 755, 739 cm$^{-1}$;

Anal. Calcd for C$_{23}$H$_{35}$O$_6$BrSi: C, 53.59; H, 6.84. Found: C, 53.35; H, 6.60.

Synthesis of cyclobutene 11d:
According to the general procedure for synthesis of cyclobutene 8a, ynoate 10d (100 mg, 0.322
mmol), KSA \textcircled{2} (101 mg, 0.407 mmol), and Me\textsubscript{3}Al (1.03 M in hexane, 0.35 mL, 0.36 mmol) gave, after purification by PTLC (hexane/EtOAc = 8/2), cyclobutene \textbf{11d} (156 mg, 86.6%) as a colorless oil.

![Cyclobutene 11d](image)

\textbf{cyclobutene 11d}

\textsuperscript{1}H NMR (acetone-\textit{d}_6, \delta)  
0.15 (s, 3H), 0.18 (s, 3H), 0.92 (s, 9H), 2.95 (td, 1H, \textit{J}_1 = 7.3, \textit{J}_2 = 14.6 Hz), 2.98 (td, 1H, \textit{J}_1 = 7.3, \textit{J}_2 = 14.6 Hz), 3.44 (s, 3H), 3.46 (s, 3H), 3.48 (s, 3H), 3.76 (s, 3H), 3.76 (t, 2H, \textit{J} = 7.3 Hz), 4.45 (s, 2H), 6.87 (d, 2H, \textit{J} = 8.7 Hz), 7.08–7.14 (m, 2H), 7.24–7.30 (m, 3H), 7.40–7.46 (m, 2H);  
\textsuperscript{13}C NMR (acetone-\textit{d}_6, \delta)  
–3.1, −3.0, 19.0, 26.3, 29.4, 51.6, 51.7, 53.0, 55.4, 67.6, 72.8, 106.4, 108.4, 114.3, 122.5, 126.7, 129.9, 130.2, 131.4. 138.9, 151.1, 160.0, 161.1, 163.7;  
IR (neat)  
3066, 2935, 2857, 1739, 1658, 1612, 1592, 1511, 1492, 1461, 1361, 1284, 1249, 1191, 1083, 1037, 914, 836, 782, 752 cm\textsuperscript{-1};  
Anal. Calcd for C\textsubscript{30}H\textsubscript{42}O\textsubscript{8}Si: C, 64.49; H, 7.58. Found: C, 64.30; H, 7.79.

\textit{Synthesis of cyclobutene 11e:}\n
According to the general procedure for synthesis of cyclobutene \textbf{8a}, alkyne \textbf{10e} (151 mg, 0.466 mmol), KSA \textcircled{2} (147 mg, 0.592 mmol), and Me\textsubscript{3}Al (1.03 M in hexane, 0.50 mL, 0.52 mmol) gave, after purification by PTLC (hexane/EtOAc = 8/2), cyclobutene \textbf{11e} (245 mg, 91.9%) as a colorless oil.

![Cyclobutene 11e](image)

\textbf{cyclobutene 11e}

\textsuperscript{1}H NMR (acetone-\textit{d}_6, \delta)  
0.16 (s, 3H), 0.18 (s, 3H), 0.92 (s, 9H), 1.94–2.04 (m, 2H), 2.75–2.82 (m, 2H), 3.44 (s, 3H), 3.46 (s, 3H), 3.48 (s, 3H), 3.51 (t, 2H, \textit{J} = 6.4 Hz), 3.76 (s, 3H), 4.40 (s, 2H), 6.84 (d, 2H, \textit{J} = 8.7 Hz), 7.14–7.18 (m, 2H), 7.22 (d, 2H, \textit{J} = 8.7 Hz), 7.25–7.30 (m, 1H), 7.40–7.46 (m, 2H);  
\textsuperscript{13}C NMR (acetone-\textit{d}_6, \delta)  
–3.2, −3.0, 19.0, 25.6, 26.3, 28.5, 51.6, 51.8, 52.9, 55.4, 70.0, 72.9, 106.4, 108.6, 114.3, 122.5, 126.7, 129.8, 130.3, 131.8. 137.6, 151.2, 160.0, 161.2, 167.0;  
IR (neat)  
2936, 2855, 1736, 1655, 1612, 1591, 1513, 1492, 1463, 1388, 1360, 1287, 1247, 1190, 1078, 1024, 937, 838, 780, 755 cm\textsuperscript{-1};  
Anal. Calcd for C\textsubscript{31}H\textsubscript{44}O\textsubscript{8}Si: C, 65.01; H, 7.74. Found: C, 64.79; H, 7.77.
Scheme 2. Preparation of ynoate 10d.

\[ \text{PMBO} \xleftarrow{n\text{-BuLi}} \text{THF, } -78\, ^\circ\text{C} \xrightarrow{\text{ClCO}_2\text{Ph}} \text{10d} \]

**Synthesis of alkyne 10d:**
To a mixture of alkyne ii (2.45 g, 12.9 mmol) in THF (60 mL) was added n-BuLi (1.60 M in hexane, 8.5 mL, 14 mmol) at −78 °C. After 1 h, ClCO₂Ph (2.00 g, 12.8 mmol) in THF (5 mL) was added to the mixture, and the reaction was stirred for further 1 h. The reaction was stopped by adding sat. NH₄Cl. The products were extracted with EtOAc and combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 9/1) to give ynoate 10d (3.50 g, 87.6%) as a colorless oil.

alkyne 10d
\[ ^1\text{H NMR (CDCl}_3, \delta) \]
2.69 (t, 2H, J = 7.3 Hz), 3.65 (t, 2H, J = 7.3 Hz), 3.80 (s, 3H), 4.51 (s, 2H), 6.86–6.94 (m, 2H), 7.10–7.16 (m, 2H), 7.23–7.34 (m, 3H), 7.35–7.44 (m, 2H);
\[ ^13\text{C NMR (CDCl}_3, \delta) \]
20.4, 55.3, 66.5, 72.8, 73.5, 88.8, 113.9, 121.4, 126.3, 129.4, 129.5, 129.7, 150.1, 151.8, 159.4; IR (neat) 3064, 3041, 3002, 2955, 2935, 2913, 2838, 2865, 2236, 1728, 1612, 1589, 1513, 1491, 1457, 1421, 1362, 1328, 1302, 1234, 1190, 1161, 1097, 1043, 1004, 949, 913, 822, 745 cm⁻¹;
Anal. Calcd for C₁₉H₁₈O₄: C, 73.53; H, 5.85. Found: C, 73.29; H, 6.15.

Scheme 3. Preparation of ynoate 10c and 10e.

\[ \text{PMBO} \xrightarrow{\text{as above}} \text{10e} \]

**Synthesis of alkyne 10e:**
According to the general procedure for synthesis of alkyne 10d, alkyne iii (1.31 g, 6.41 mmol),
ClCO₂Ph (1.12 g, 7.15 mmol), and n-BuLi (1.60 M in hexane, 4.1 mL, 6.6 mmol) gave, after purification by silica-gel flash column chromatography (hexane/EtOAc = 9/1), alkyne 10e (1.83 g, 88.0%) as a colorless oil.

alkyne 10e

$^1$H NMR (CDCl₃, δ)
1.89 (tt, 2H, J₁ = 6.1, J₂ = 7.0 Hz), 2.52 (t, 2H, J = 7.0 Hz), 3.55 (t, 2H, J = 6.1 Hz), 3.79 (s, 3H), 4.45 (s, 2H), 6.86–6.92 (m, 2H), 7.10–7.15 (m, 2H), 7.22–7.30 (m, 3H), 7.36–7.44 (m, 2H);

$^{13}$C NMR (CDCl₃, δ)
15.8, 27.7, 55.3, 67.9, 72.7, 72.9, 91.6, 113.8, 121.4, 126.3, 129.3, 129.5, 130.3, 150.1, 152.0, 159.2;

IR (neat)
3063, 3041, 3001, 2954, 2934, 2858, 2230, 1728, 1612, 1590, 1513, 1490, 1457, 1442, 1363, 1301, 1232, 1190, 1162, 1102, 1063, 1038, 1001, 915, 820, 741 cm⁻¹;

Anal. Calcd for C₂₀H₂₀O₄: C, 74.06; H, 6.21. Found: C, 74.27; H, 6.32.

Synthesis of alkyne iv:

To a solution of ester 10e (1.12 g, 3.45 mmol) in CH₂Cl₂ (2 mL) and H₂O (1 mL) was added DDQ (812 mg, 3.57 mmol) at 0 °C. After warmed to room temperature, and stirred for further 2 h, the reaction was stopped by adding sat. aq. NaHCO₃. The products were extracted with EtOAc and combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 7/3) to give alcohol iv (547 mg, 77.6%) as a colorless oil.

alcohol iv

$^1$H NMR (CDCl₃, δ)
1.88 (quint, 2H, J = 7.0 Hz), 2.55 (t, 2H, J = 7.0 Hz), 3.55 (t, 1H, J = 6.0 Hz), 3.78 (dt, 2H, J₁ = 6.0, J₂ = 7.0 Hz), 7.10–7.17 (m, 2H), 7.23–7.28 (m, 1H), 7.36–7.43 (m, 2H);

$^{13}$C NMR (CDCl₃, δ)
15.2, 30.0, 60.8, 72.8, 91.6, 121.3, 126.3, 129.5, 149.9, 152.0;

IR (neat)
3495, 2954, 2881, 2232, 1728, 1590, 1490, 1457, 1425, 1326, 1235, 1190, 1161, 1047, 1001, 915, 838, 742 cm⁻¹;

Anal. Calcd for C₁₂H₁₂O₃: C, 70.57; H, 5.92. Found: C, 70.42; H, 5.98.
Synthesis of mesylate v

To a mixture of alcohol iv (143 mg, 0.700 mmol) and Et₃N (121 mg, 1.20 mmol) in CH₂Cl₂ (3 mL) was added MsCl (91 mg, 0.794 mmol) in CH₂Cl₂ (1 mL) at 0 °C. After 15 min, the reaction was stopped by adding water. The products were extracted with EtOAc and combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 5/5) to give mesylate v (157 mg, 79.4%) as a colorless oil.

\[
\begin{align*}
\text{mesylate v} \\
\text{\textsuperscript{1}H NMR (CDCl₃, } \delta \text{)} \\
1.89 \text{ (quint, 2H, } J = 6.3 \text{ Hz), 2.60 \text{ (t, 2H, } J = 6.3 \text{ Hz), 3.06 \text{ (s, 3H), 4.36 \text{ (t, 2H, } J = 6.3 \text{ Hz),}} \\
7.10–7.17 \text{ (m, 2H), 7.23–7.30 \text{ (m, 1H), 7.37–7.44 \text{ (m, 2H);}}}
\text{\textsuperscript{13}C NMR (CDCl₃, } \delta \text{)} \\
15.3, 27.0, 37.4, 67.7, 73.8, 89.3, 121.4, 126.4, 129.6, 150.0, 151.7; \\
\text{IR (neat)} \\
3029, 2940, 2235, 1727, 1590, 1489, 1355, 1236, 1190, 1175, 972, 929, 832, 748 \text{ cm}^{-1}; \\
\text{Anal. Calcd for C₁₃H₁₄O₅S: C, 55.31; H, 5.00. Found: C, 55.15; H, 5.21.}
\end{align*}
\]

Synthesis of alkyne 10c

To a solution of mesylate v (99.2 mg, 0.351 mmol) in acetone (20 mL) was added LiBr (152 mg, 1.75 mmol) at 0 °C. The mixture was heated under reflux conditions for 1 h. The reaction was stopped by adding water, and the products were extracted with EtOAc and combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 7/3) to give bromide 10c (89.1 mg, 94.9%) as a colorless oil.

\[
\begin{align*}
ynoate 10c \\
\text{\textsuperscript{1}H NMR (CDCl₃, } \delta \text{)} \\
2.15 \text{ (quint, 2H, } J = 6.5 \text{ Hz), 2.62 \text{ (t, 2H, } J = 6.5 \text{ Hz), 3.52 \text{ (t, 2H, } J = 6.5 \text{ Hz),}} \\
7.10–7.16 \text{ (m, 2H), 7.23–7.30 \text{ (m, 1H), 7.36–7.44 \text{ (m, 2H);}}}
\text{\textsuperscript{13}C NMR (CDCl₃, } \delta \text{)} \\
17.5, 30.2, 31.6, 73.5, 89.8, 121.4, 126.4, 129.6, 150.1, 151.8; \\
\text{IR (neat)} \\
3064, 2965, 2232, 1728, 1590, 1489, 1456, 1435, 1233, 1190, 1161, 1071, 1038, 1002, 740 \text{ cm}^{-1};
\end{align*}
\]
Synthesis of cyclobutenone 12:
To a solution of cyclobutene 11b (456 mg, 0.970 mmol) in CH₂Cl₂ (7.0 mL) and H₂O (0.5 mL) was added BF₃·OEt₂ (451 mg, 3.19 mmol) in CH₂Cl₂ (3.0 mL) at −78 °C. After the mixture was warmed to −10 °C and stirred for further 0.5 h, the reaction was quenched by adding sat. aq. NaHCO₃. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 20/1) to give cyclobutenone 12 (266 mg, 84.7%). Recrystallization from Et₂O gave 12 as colorless prisms.

1H NMR (acetone-d₆, δ) 3.55 (s, 6H), 7.29–7.35 (m, 3H), 7.45–7.52 (m, 2H), 7.60–7.66 (m, 2H), 7.70–7.76 (m, 1H), 8.38–8.44 (m, 2H);

13C NMR (acetone-d₆, δ) 54.2, 118.0, 122.5, 127.1, 129.2, 129.9, 130.3, 132.5, 135.7, 138.1, 151.2, 158.9, 183.1, 188.8;

IR (ATR) 3066, 3000, 2942, 2838, 1774, 1735, 1585, 1488, 1450, 1346, 1303, 1253, 1195, 1141, 1103, 1056, 995, 921, 898, 840, 798, 771, 725 cm⁻¹;

Anal. Calcd for C₁₉H₁₆O₅: C, 70.36; H, 4.97. Found: C, 70.16; H, 4.98.

Figure 2. X-ray structure of 12[7]

[7] CCDC-709482 (12) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Synthesis of cyclobutene 13:
To a solution of cyclobutene 11b (150 mg, 0.319 mmol) in THF (5.0 mL) was added LiAlH₄ (20 mg, 0.52 mmol) at 0 °C. After 15 min, the reaction was quenched by adding sat. aq. NaHCO₃. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 7/3) to give cyclobutene 13 (106 mg, 87.4%) as a colorless oil.

\[
\text{OSi}t\text{-BuMe}_2
\]
\[
\text{OMe}
\]
\[
\text{OMe}
\]
\[
\text{Ph}
\]
\[
\text{HO}
\]
cyclobutene 15

\[
\begin{align*}
\text{HO} & \quad \text{OSi}t\text{-BuMe}_2 \\
\text{Ph} & \quad \text{OMe} \\
\text{OMe} & \quad \text{OMe}
\end{align*}
\]

1H NMR (acetone-d₆, δ)
0.17 (s, 6H), 0.92 (s, 9H), 3.35 (s, 3H), 3.47 (s, 6H), 4.05–4.08 (m, 1H), 4.37–4.78 (m, 2H), 7.28–7.40 (m, 3H), 7.72–7.78 (m, 2H);

13C NMR (acetone-d₆, δ)
−2.90, −2.89, 19.0, 26.3, 52.2, 52.7, 55.7, 107.4, 109.8, 128.9, 129.0, 129.4, 133.9, 145.8, 148.4;

IR (neat)
3448, 3056, 2937, 2856, 2834, 1656, 1573, 1494, 1463, 1274, 1253, 1211, 1178, 1139, 1085, 1002, 993, 921, 892, 869, 836, 779 cm⁻¹;

Anal. Calcd for C₂₀H₃₂O₅Si: C, 63.12; H, 8.48. Found: C, 62.90; H, 8.70.

Synthesis of cyclobutenone 14:
To a solution of cyclobutene 13 (88.0 mg, 0.231 mmol) in CH₃CN (3.0 mL) was added sat. aq. KF (0.1 mL) and n-Bu₄NCl (4.8 mg, 0.0173 mmol) at room temperature. After 24 h, the reaction was stopped by adding water. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 5/5) to give cyclobutenone 14 (47.2 mg, 87.2%) as a pale yellow oil.

\[
\begin{align*}
\text{HO} & \quad \text{O} \\
\text{Ph} & \quad \text{OMe} \\
\text{OMe} & \quad \text{OMe}
\end{align*}
\]
cyclobutenone 14

1H NMR (acetone-d₆, δ)
3.44 (s, 6H), 4.44–4.52 (m, 3H), 7.50–7.60 (m, 3H), 7.97–8.02 (m, 2H);

13C NMR (acetone-d₆, δ)
53.7, 118.1, 129.6, 130.4, 130.5, 132.6, 152.8, 174.8, 193.9;

IR (neat)
3472, 3064, 2998, 2944, 2837, 1754, 1613, 1573, 1494, 1448, 1346, 1337, 1317, 1302, 1254, 1205, 1171, 1096, 1060, 1026, 1000, 928, 888, 771, 741 cm⁻¹;


Synthesis of cyclobutenedione 15:
To a solution of cyclobutene 14 (37.3 mg, 0.159 mmol) in CH₂Cl₂ (1.5 mL) and H₂O (0.05 mL) was added BF₃·OEt₂ (0.05 mL, 0.40 mmol) at 0 °C. After 0.5 h, the reaction was quenched by adding...
sat. aq. NaHCO₃. The products were extracted with EtOAc (x3), and the combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 5/5) to give cyclobutenedione 15 (23.7 mg, 79.1%). Recrystallization from hexane/Et₂O gave 15 as yellow needles. Mp. 101.9–102.6 °C.

![Cyclobutenedione 15](image)

**Cyclobutenedione 15**

1H NMR (acetone-**d₆**, δ)
4.91 (br s, 1H), 5.10 (s, 2H), 7.58–7.70 (m, 3H), 8.23–8.28 (m, 2H);

13C NMR (acetone-**d₆**, δ)
57.3, 129.1, 130.0, 130.8, 134.2, 190.5, 196.6, 196.7, 197.8;

IR (ATR)
3472, 3065, 2894, 1780, 1761, 1597, 1581, 1568, 1491, 1448, 1388, 1334, 1312, 1294, 1214, 1184, 1154, 1105, 1085, 1056, 999, 941, 873, 814, 764 cm⁻¹;

Anal. Calcd for C₁₁H₈O₃: C, 70.21; H, 4.29. Found: C, 69.99; H, 4.03.