Supporting Information

A Domino Pericyclic Route to Polysubstituted Salicylic Acid Derivatives: Four Sequential Processes from Enynones and Ketene Silyl Acetals

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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. {^{1}H NMR and {^{13}C NMR were measured on a JEOL JNM lambda-400, a JEOL JNM ECA-300, a JEOL JNM ECA-400, and a Bruker DRX-500 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.
Preparation of diene 22:

\[
\begin{align*}
\text{PhO} & \quad \text{OSi-BuMe}_2 \\
\text{Ph} & \quad \text{OMe} \\
\text{Ph} & \quad \text{OMe} \\
\text{Ph} & \quad \text{OMe} \\
\text{LiAlH}_4 & \quad \text{THF, 0 °C} \\
\text{TPAP, NMO} & \quad \text{CH}_2\text{Cl}_2 \quad 87\% \\
\text{EtOAc} & \quad \times 3 \\
\text{Na}_2\text{SO}_4 & \quad \text{dried} \\
\text{vacuo} & \quad \text{concentrated} \\
\text{PTLC} & \quad \text{hexane/EtOAc = 7/3} \\
\text{Ph} & \quad \text{OMe} \\
\text{Ph} & \quad \text{OMe} \\
\text{Ph} & \quad \text{OMe} \\
\text{Ph} & \quad \text{OMe} \\
\end{align*}
\]

Synthesis of cyclobutene i:
To a solution of cyclobutene 21 1) (150 mg, 0.319 mmol) in THF (5.0 mL) was added LiAlH₄ (20 mg, 0.53 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 i (106 mg, 87.4%) as a colorless oil.

\[
\begin{align*}
\text{Cyclobutene } i \\
\text{H NMR (acetone-}d_6, \delta) \\
0.17 & \text{ (s, 6H), 0.92 (s, 9H), 3.35 (s, 3H), 3.47 (s, 6H), 4.05–4.08 (m, 1H), 4.37–4.78 (m, 2H),} \\
7.28–7.40 & \text{ (m, 3H), 7.72–7.78 (m, 2H);} \\
\text{C NMR (acetone-}d_6, \delta) \\
–2.90 & \text{, } –2.89, 19.0, 26.3, 52.2, 52.7, 55.7, 107.4, 109.8, 128.9, 129.0, 129.4, 133.9, 145.8, 148.4; \\
\text{IR (neat)} \\
3448 & \text{, 3056, 2937, 2856, 2834, 1656, 1573, 1494, 1463, 1274, 1253, 1211, 1178, 1139, 1085, 1002,} \\
993 & \text{, 921, 892, 869, 836, 779 cm}^{-1}; \\
\text{Anal. Calcd for } C_{20}H_{32}O_5Si: C, 63.12; H, 8.48. \text{ Found: C, 62.90; H, 8.70.}
\end{align*}
\]

Synthesis of aldehyde ii:
To a stirred mixture of allyl alcohol i (24.4 mg, 0.0641 mmol), NMO (18.0 mg, 0.154 mmol), and 4 Å molecular sieves (60 mg) in CH₂Cl₂ (2.0 mL) was added TPAP (3.8 mg, 0.011 mmol) at room temperature. After stirred for 12 h, the reaction mixture was filtered through celite pad. The filtrate was purified by PTLC (hexane/EtOAC = 7/3) to afford ii (20.2 mg, 83.2%) as a colorless oil.

aldehyde ii

1H NMR (acetone-d$_6$, $\delta$)
0.14 (s, 3H), 0.18 (s, 3H), 0.93 (s, 9H), 3.40 (s, 3H), 3.42 (s, 3H), 3.48 (s, 3H), 7.47–7.55 (m, 3H), 7.94–7.97 (m, 2H), 10.1 (s, 1H);

13C NMR (acetone-d$_6$, $\delta$)

IR (neat)
2943, 2856, 1679, 1572, 1492, 1359, 1261, 1213, 1116, 1060, 1001, 990, 891, 835, 804, 779 cm$^{-1}$;

Anal. Calcd for C$_{20}$H$_{30}$O$_5$Si: C, 63.46; H, 7.99. Found: C, 63.22; H, 7.97.

Synthesis of alcohol iii:
To a solution of 2-bromo-cis-2-butene (86 mg, 96% purity, 0.61 mmol) in Et$_2$O (1.2 mL) was slowly added $t$-BuLi (1.48 M in pentane, 0.47 ml, 0.70 mmol) at –78 °C, and the reaction mixture was further stirred for 1 h; to the stirred solution was added aldehyde ii (105 mg, 0.278 mmol) in Et$_2$O (2.0 mL). After 10 min, the reaction was quenched with water. The products were extracted with EtOAc (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/EtOAc = 97/3) to give less polar product iii (47.6 mg, 39.5%) and more polar product iii (49.8 mg, 41.3%).

alcohol iii (less polar)

1H NMR (acetone-d$_6$, $\delta$)
0.21 (s, 3H), 0.22 (s, 3H), 0.95 (s, 9H), 1.56 (d, 3H, $J = 6.4$ Hz), 1.63 (s, 3H), 3.30 (s, 3H), 3.41 (s, 3H), 3.46 (s, 3H), 4.03 (d, 1H, $J = 4.2$ Hz), 5.00 (d, 1H, $J = 4.2$ Hz), 5.67 (q, 1H, $J = 6.4$ Hz), 7.25–7.36 (m, 3H), 7.78–7.82 (m, 2H);

13C NMR (acetone-d$_6$, $\delta$)
–2.6, –2.5, 13.1, 13.3, 19.2, 26.6, 51.9, 52.6, 52.9, 73.3, 108.0, 109.6, 122.2, 128.6, 128.9, 129.9, 133.9, 137.1, 145.3, 149.9;

IR (neat)
3468, 2936, 1494, 1471, 1387, 1360, 1248, 1210, 1171, 1080, 1029, 992, 894, 835, 805, 778 cm$^{-1}$;

Anal. Calcd for C$_{24}$H$_{38}$O$_5$Si: C, 66.32; H, 8.81. Found: C, 66.41; H, 8.80.

alcohol iii (more polar)

1H NMR (acetone-d$_6$, $\delta$)
0.17 (s, 3H), 0.20 (s, 3H), 0.91 (s, 9H), 1.53 (d, 3H, J = 6.9 Hz), 1.58 (s, 3H), 3.32 (s, 3H), 3.42 (s, 3H), 3.54 (s, 3H), 4.18 (d, 1H, J = 4.6 Hz), 4.87 (d, 1H, J = 4.6 Hz), 5.66 (q, 1H, J = 6.9 Hz), 7.24–7.33 (m, 3H), 7.80–7.84 (m, 2H);

$^{13}$C NMR (acetone-$d_6$, δ)
–2.5, 13.1, 13.3, 18.9, 26.5, 51.8, 52.7, 53.2, 73.1, 108.0, 109.7, 122.3, 128.4, 128.9, 130.2, 133.7, 136.7, 146.1, 149.3;

IR (neat)
3479, 2937, 2856, 1493, 1471, 1387, 1360, 1247, 1208, 1172, 1080, 1039, 991, 885, 835, 808, 777 cm$^{-1}$;

Anal. Calcd for C$_{24}$H$_{38}$O$_5$Si: C, 66.32; H, 8.81. Found: C, 66.21; H, 8.69.

Synthesis of dienone 22:
To a stirred mixture of alcohol iii (33.3 mg, 0.0766 mmol), NMO (23.0 mg, 0.196 mmol), and 4 Å molecular sieves (72 mg) in CH$_2$Cl$_2$ (2.0 mL) was added TPAP (5.2 mg, 0.015 mmol) at room temperature. After stirred for 10 h, the reaction mixture was filtered through celite pad. The filtrate was purified by PTLC (hexane/EtOAC = 7/3) to afford 22 (28.2 mg, 85.1%) as a colorless oil.

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Dienone 22

$^1$H NMR (acetone-$d_6$, δ)
0.05 (s, 3H), 0.16 (s, 3H), 0.90 (s, 9H), 1.76 (qd, 3H, J$_1$ = 1.0, J$_2$ = 6.9 Hz), 1.79–1.81 (m, 3H), 3.43 (s, 3H), 3.44 (s, 3H), 3.52 (s, 3H), 6.88 (qq, 1H, J$_1$ = 1.4, J$_2$ = 6.9 Hz), 7.31–7.47 (m, 5H);

$^{13}$C NMR (acetone-$d_6$, δ)
–3.1, –2.8, 10.3, 15.1, 19.0, 26.5, 52.3, 52.5, 53.7, 108.8, 109.3, 128.9, 129.3, 130.1, 132.8, 139.0, 145.4, 146.4, 148.3, 194.7;

IR (neat)
2937, 2855, 1633, 1493, 1471, 1387, 1360, 1247, 1208, 1172, 1080, 1039, 991, 885, 835, 808, 777 cm$^{-1}$;


Preparation of dinone 24:

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alcohol iv (less polar)\(^2\)

\(^1\)H NMR (acetone-\(d_6\), \(\delta\))
0.22 (s, 3H), 0.25 (s, 3H), 0.96 (s, 9H), 2.16–2.23 (m, 2H), 2.63 (t, 2H, \(J = 7.9\) Hz), 3.32 (s, 3H),
3.43 (s, 3H), 3.50 (s, 3H), 3.97 (d, 1H, \(J = 5.8\) Hz), 5.67 (d, 1H, \(J = 5.8\) Hz), 6.36 (t, 1H, \(J = 4.8\) Hz),
7.10–7.30 (m, 6H), 7.58–7.65 (m, 3H);
\(^1\)C NMR (acetone-\(d_6\), \(\delta\))
-2.5, -2.4, 19.2, 23.8, 26.6, 28.5, 51.9, 52.7, 53.2, 68.4, 108.2, 109.6, 124.6, 127.0, 127.6, 128.2,
128.7, 128.9, 129.5, 129.7, 134.0, 134.3, 137.4, 137.6, 145.6, 150.2;
IR (neat)
3594, 2933, 2855, 2833, 1491, 1462, 1387, 1360, 1248, 1210, 1174, 1080, 1034, 990, 923, 890, 835,
806, 778, 746, 732 cm\(^{-1}\);
Anal. Calcd for C\(_{30}\)H\(_{40}\)O\(_5\)Si: C, 70.83; H, 7.93. Found: C, 70.69; H, 7.78.

alcohol iv (more polar)

\(^1\)H NMR (acetone-\(d_6\), \(\delta\))
0.14 (s, 3H), 0.21 (s, 3H), 0.91 (s, 9H), 2.08–2.23 (m, 2H), 2.50–2.63 (m, 2H), 3.34 (s, 3H), 3.41 (s, 3H),
3.61 (s, 3H), 4.31 (d, 1H, \(J = 5.3\) Hz), 5.57 (d, 1H, \(J = 4.0\) Hz), 6.30 (t, 1H, \(J = 4.6\) Hz),
7.04–7.13 (m, 3H), 7.20–7.27 (m, 3H), 7.52 (d, 1H, \(J = 7.2\) Hz), 7.65–7.69 (m, 2H);
\(^1\)C NMR (acetone-\(d_6\), \(\delta\))
-2.6, -2.5, 19.0, 23.7, 26.6, 28.4, 51.9, 52.7, 53.4, 66.7, 108.1, 109.8, 124.4, 126.8, 127.4, 128.1,
128.2, 128.4, 128.9, 130.0, 133.7, 134.4, 136.7, 137.4, 147.4, 149.2;
IR (neat)
3460, 2936, 2884, 2855, 1490, 1470, 1449, 1388, 1359, 1248, 1209, 1174, 1083, 1001, 935, 887,
838, 779, 735 cm\(^{-1}\);

\(^2\) Vinyllithium A was generated by halogen–lithium exchange of iodoalkene a, \(^i\) prepared from
1-tetralone.

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Domino pericyclic reaction of dienones to salicylic acid derivatives; 
Synthesis of benzene 9 starting from dienone 6 (Method A): 
A solution of dienone 6 (48.0 mg, 0.118 mmol) in mesitylene (3.0 mL) and 2,6-lutidine (0.5 mL) was heated at 165 °C for 10 h. After evaporation of the solvent, the residue was purified by PTLC (hexane/EtOAC = 9/1) to give 9 (35.4 mg, 80.1%) as a colorless oil.

Synthesis of benzene 9 by reaction of enynone 5 and KSA 2a (Method B): 
A mixture of enynone 5 (37.0 mg, 0.237 mmol) and KSA 2a (70.2 mg, 0.283 mmol) was heated at 60 °C for 1 h. After diluted in mesitylene (2.4 mL), the mixture was heated at 165 °C for 14 h. The crude product was purified by PTLC (hexane/CH₂Cl₂/Et₂O = 6/2/2) to give 9 (66.4 mg, 75.2%) as a colorless oil.

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ester 7

$^1$H NMR (acetone-$d_6$, $\delta$)
0.20 (s, 3H), 1.06 (s, 9H), 3.48 (s, 2H), 3.62 (s, 3H), 3.68 (s, 3H), 7.07 (d, 1H, $J = 16.2$ Hz),
7.28–7.44 (m, 3H), 7.51–7.63 (m, 2H), 8.11 (d, 1H, $J = 16.2$ Hz);

$^{13}$C NMR (acetone-$d_6$, $\delta$)
−3.2, 19.1, 26.3, 33.7, 51.7, 51.9, 110.9, 124.4, 128.1, 129.72, 129.77, 136.3, 137.0, 160.5, 168.3, 172.1;

IR (neat)
3025, 2952, 2932, 2887, 2859, 1743, 1710, 1626, 1581, 1569, 1463, 1434, 1312, 1285, 1259, 1191, 1169, 1116, 1055, 975, 933, 841, 828, 810, 784, 756 cm$^{-1}$;

Anal. Calcd for C$_{21}$H$_{30}$O$_5$Si: C, 64.58; H, 7.74. Found: C, 64.79; H, 7.95.

Cyclohexadiene 8

$^1$H NMR (acetone-$d_6$, $\delta$)
0.12 (s, 6H), 0.90 (s, 9H), 3.09 (s, 3H), 3.25 (s, 3H), 3.77 (s, 3H), 3.81 (d, 1H, $J = 6.6$ Hz), 5.28 (d, 1H, $J = 6.6$ Hz), 6.24 (s, 1H), 7.16–7.42 (m, 3H), 7.30–7.36 (m, 2H);

$^{13}$C NMR (acetone-$d_6$, $\delta$)
−4.6, −4.5, 18.6, 26.0, 49.3, 49.52, 49.54, 52.3, 100.5, 112.6, 127.7, 128.9, 129.6, 134.9, 135.5, 139.1, 144.5, 166.5;

IR (neat)
2952, 2858, 1737, 1482, 1379, 1256, 1123, 1076, 1053, 893, 840, 781 cm$^{-1}$;

Anal. Calcd for C$_{22}$H$_{32}$O$_5$Si: C, 65.31; H, 7.74. Found: C, 65.52; H, 8.18.

Synthesis of benzene 13:
According to the general procedure of 9 (Method B), ynone 10 (37.5 mg, 0.346 mmol) and KSA 2a (131 mg, 0.527 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave 13 (79.8 mg, 70.9%) as a colorless oil.

Benzene 13

$^1$H NMR (CDCl$_3$, $\delta$)
0.01 (s, 6H), 1.05 (s, 9H), 2.14 (s, 3H), 2.15 (s, 3H), 3.80 (s, 3H), 3.85 (s, 3H), 7.05 (s, 1H);

$^{13}$C NMR (CDCl$_3$, $\delta$)
−4.4, 12.7, 14.0, 18.3, 25.8, 51.8, 55.7, 109.3, 120.3, 130.8, 131.6, 146.3, 151.6, 168.3;

IR (neat)
2950, 2858, 1729, 1601, 1578, 1432, 1409, 1361, 1335, 1266, 1227, 1195, 1173, 1114, 1093, 1010, 963, 882, 841, 827, 814, 778, 731 cm\(^{-1}\);
Anal. Calcd for C\(_{17}\)H\(_{28}\)O\(_4\)Si: C, 62.92; H, 8.70. Found: C, 63.13; H, 8.66.

**Synthesis of benzene 14:**
According to the general procedure of 9 (Method B), ynone 11 (38.4 mg, 0.282 mmol) and KSA 2a (106 mg, 0.426 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave 14 (65.4 mg, 66.1%) as a colorless oil.

![Image of benzene 14](image)

\(^{1}\)H NMR (CDCl\(_3\), \(\delta\))
0.05 (s, 6H), 1.03 (s, 9H), 1.64–1.77 (m, 4H), 2.57–2.70 (m, 4H), 3.79 (s, 3H), 3.84 (s, 3H), 6.97 (s, 1H);
\(^{13}\)C NMR (CDCl\(_3\), \(\delta\))
–4.0, 18.4, 22.0, 22.3, 23.7, 25.0, 25.8, 51.7, 55.4, 108.0, 119.5, 131.9, 132.3, 146.3, 151.4, 168.3;
IR (neat)
2932, 2857, 1730, 1601, 1577, 1463, 1448, 1432, 1411, 1332, 1271, 1250, 1224, 1188, 1162, 1103, 1083, 1063, 989, 960, 939, 895, 882, 841, 827, 813, 788, 778, 728 cm\(^{-1}\);

**Synthesis of cyclohexadiene 15:**
A mixture of dienone 5 (48.0 mg, 0.307 mmol) and KSA 2b (98.7 mg, 0.452 mmol) was heated at 60 ℃ for 1 h. After diluted in xylene (3.0 mL), the reaction was heated at 140 ℃ for 3 h. Evaporation of the solvents gave the crude product, which was purified by PTLC (hexane/CH\(_2\)Cl\(_2\)/Et\(_2\)O = 70/15/15) to give 15-cis (84.7 mg, 73.6%) and 15-trans (14.1 mg, 12.2%).

![Image of cyclohexadiene 15](image)

1H NMR (acetone-\(d_6\), \(\delta\))
0.19 (s, 3H), 0.20 (s, 3H), 0.93 (s, 9H), 3.25 (s, 3H), 3.73 (s, 3H), 3.84 (dd, 1H, \(J_1 = 5.4\), \(J_2 = 7.8\) Hz), 4.28 (dd, 1H, \(J_1 = 3.4\), \(J_2 = 7.8\) Hz), 5.24 (d, 1H, \(J = 5.4\) Hz), 6.45 (d, 1H, \(J = 3.4\) Hz) 7.15–7.35 (m, 5H);
\(^{13}\)C NMR (acetone-\(d_6\), \(\delta\))
–5.3, 17.8, 25.1, 43.1, 51.2, 56.5, 77.5, 107.9, 126.6, 127.8, 129.4, 131.4, 136.1, 138.1, 146.5, 165.5;
IR (neat)
2962, 2903, 2858, 1734, 1647, 1599, 1261, 1091, 1019, 799 cm\(^{-1}\);
The stereochemistry of \textbf{15-cis} was determined on the basis of the observed NOE shown below.

\[
\begin{align*}
\text{H}_a: & \quad 3.84 \text{ ppm}, \text{H}_b: \quad 7.33 \text{ ppm.}
\end{align*}
\]

cyclohexadiene \textbf{15-trans}

\[^1\text{H} \text{NMR (acetone-}d_6, \delta)\]
0.218 (s, 3H), 0.223 (s, 3H), 1.00 (s, 9H), 2.55 (dd, 1H, \(J = 5.6, 18.3 \text{ Hz})\), 3.27 (s, 3H), 3.28 (dd, 1H, \(J = 2.2\), 18.3 Hz), 3.69 (s, 3H), 4.38 (dd, 1H, \(J = 2.2, 5.6 \text{ Hz})\), 6.39 (s, 1H), 7.31–7.42 (m, 3H), 7.58–7.65 (m, 2H);

\[^13\text{C} \text{NMR (acetone-}d_6, \delta)\]
–3.9, –3.8, 18.9, 26.1, 28.9, 51.1, 55.5, 73.0, 105.0, 125.8, 126.8, 129.3, 129.6, 139.2, 144.0, 155.6, 167.5;

IR (neat) 2930, 2858, 1713, 1637, 1580, 1435, 1372, 1297, 1251, 1209, 1165, 1087, 1075, 994, 946, 919, 884, 833, 782 cm\(^{-1}\);


The stereochemistry of \textbf{15-trans} was determined on the basis of the observed NOE shown below.

\[
\begin{align*}
\text{H}_a: & \quad 7.61 \text{ ppm, H}_b: \quad 2.55 \text{ ppm, H}_c: \quad 3.27 \text{ ppm, H}_d: \quad 3.28 \text{ ppm.}
\end{align*}
\]

\textit{Synthesis of cyclohexadiene 16:} According to the general procedure of 15, ynone 5 (32.3 mg, 0.235 mmol) and KSA 2c (63.2 mg, 0.312 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave 16 (46.1 mg, 62.2\%) as a colorless oil.
cyclohexadiene 16

$^1$H NMR (acetone-$d_6$, $\delta$)
0.196 (s, 3H), 0.199 (s, 3H), 0.94 (s, 9H), 1.26 (t, 3H, J = 7.0 Hz), 2.35 (ddd, 1H, $J_1 = 4.6$, $J_2 = 11.7$, $J_3 = 17.3$ Hz), 2.57 (ddd, 1H, $J_1 = 4.6$, $J_2 = 8.0$, $J_3 = 17.3$ Hz), 3.69 (ddd, 1H, $J_1 = 4.1$, $J_2 = 8.0$, $J_3 = 11.7$ Hz), 4.16 (q, 2H, $J = 7.0$ Hz), 5.07 (d, 1H, $J = 4.1$ Hz), 6.56 (t, 1H, $J = 4.6$ Hz), 7.18–7.35 (m, 5H);
$^{13}$C NMR (acetone-$d_6$, $\delta$)
–4.5, –4.4, 14.5, 18.7, 26.0, 32.9, 40.2, 60.9, 108.9, 127.3, 128.2, 129.3, 132.7, 135.8, 145.6, 147.6, 165.9;
IR (neat)
2955, 2931, 2896, 2858, 1729, 1643, 1601, 1472, 1382, 1363, 1276, 1251, 1214, 1073, 932, 840, 780, 756, 700 cm$^{-1}$;
Anal. Calcd for C$_{21}$H$_{30}$O$_3$Si: C, 70.35; H, 8.43. Found: C, 70.25; H, 8.41.

Synthesis of cyclohexadiene 17:
According to the general procedure of 15, ynone 10 (34.7 mg, 0.321 mmol) and KSA 2b (89.7 mg, 0.411 mmol), after purification by PTLC (hexane/CH$_2$Cl$_2$/Et$_2$O = 70/15/15), gave 17 (58.8 mg, 56.1%) as a colorless oil.

cyclohexadiene 17

$^1$H NMR (acetone-$d_6$, $\delta$)
–0.03 (s, 3H), 0.06 (s, 3H), 0.83 (d, 3H, J = 7.0 Hz), 0.93 (s, 9H), 1.72 (s, 3H), 2.38 (dquint, 1H, $J_1 = 1.7$, $J_2 = 7.0$ Hz), 3.34 (s, 3H), 3.68 (s, 3H), 4.23 (dd, 1H, $J_1 = 2.2$, $J_2 = 7.0$ Hz), 6.30 (dd, 1H, $J_1 = 1.7$, $J_2 = 2.2$ Hz);
$^{13}$C NMR (acetone-$d_6$, $\delta$)
–4.5, –4.7, 8.3, 15.0, 18.5, 26.0, 37.8, 51.7, 56.5, 79.6, 121.5, 130.8, 137.3, 140.0, 166.3;
IR (neat)
2951, 2930, 2899, 2857, 1734, 1650, 1603, 1472, 1462, 1435, 1377, 1366, 1330, 1298, 1258, 1195, 1130, 1100, 1065, 1054, 1014, 981, 941, 890, 840, 785, 743 cm$^{-1}$;

$^{#3}$The stereochemistry of 17 was determined on the basis of the observed NOE shown below.
Synthesis of cyclohexadiene 18:
According to the general procedure of 15, ynone 11 (28.0 mg, 0.209 mmol) and KSA 2b (112 mg, 0.513 mmol), after purification by PTLC (hexane/CH₂Cl₂/Et₂O = 8/1/1), gave 18 (36.6 mg, 49.8%) as a colorless oil.

1H NMR (acetone-d₆, δ)
0.02 (s, 3H), 0.03 (s, 3H), 0.94 (s, 9H), 1.14–1.52 (m, 3H), 1.71–1.85 (m, 4H), 2.37–2.44 (m, 1H), 2.79–2.84 (m, 1H), 3.31 (s, 3H), 3.69 (s, 3H), 3.93 (dd, 1H, J₁ = 4.1, J₂ = 7.6 Hz), 6.40 (d, 1H, J = 4.1 Hz);

13C NMR (acetone-d₆, δ)
–4.8, –4.6, 18.6, 25.95, 26.04, 26.1, 27.3, 27.8, 42.4, 51.8, 56.7, 75.3, 123.7, 132.0, 133.0, 137.6, 167.0;
IR (neat)
2930, 2858, 2859, 2740, 1734, 1642, 1587, 1437, 1363, 1257, 1172, 1004, 951, 883, 840, 780 cm⁻¹;
Anal. Calcd for C₁₉H₃₂O₄Si: C, 64.73; H, 9.15. Found: C, 64.43; H, 8.95.

Synthesis of cyclohexadiene 19:
According to the general procedure of 15, ynone 12 (36.6 mg, 0.338 mmol) and KSA 2b (100 mg, 0.458 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave 19 (66.1 mg, 59.8%) as a colorless oil.

1H NMR (CDCl₃, δ)
0.10 (s, 3H), 0.13 (s, 3H), 0.89 (s, 9H), 0.94 (s, 3H), 1.08 (s, 3H), 3.40 (s, 3H), 3.73 (s, 3H), 3.74 (d, 1H, J = 2.6 Hz), 4.79 (s, 1H), 6.59 (d, 1H, J = 2.6 Hz);

13C NMR (CDCl₃, δ)
–4.8, –4.6, 18.0, 19.7, 25.6, 27.3, 37.4, 51.8, 57.7, 84.3, 117.3, 130.4, 137.8, 143.7, 166.1;
IR (neat)
2853, 2932, 2859, 1734, 1642, 1274, 1437, 1363, 1257, 1172, 1104, 1004, 951, 883, 840, 783 cm⁻¹;
Anal. Calcd for C\textsubscript{17}H\textsubscript{30}O\textsubscript{4}Si: C, 62.54; H, 9.26. Found: C, 62.33; H, 9.43.

Synthesis of benzene 23:
According to the general procedure of 9 (Method A), dienone 22 (44.1 mg, 0.102 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave 23 (31.6 mg, 77.4\%) as a colorless oil.

\[
\text{OSi-BuMe}_2 \quad \text{CO}_2\text{Me} \\
\text{Ph} \\
\text{OMe}
\]

benzene 23
\(^1\text{H} \text{NMR (CDCl}_3, \delta\)
0.11 (s, 6H), 1.02 (s, 9H), 2.18 (s, 3H), 2.24 (s, 3H), 3.23 (s, 3H), 3.40 (s, 3H), 7.27–7.38 (m, 5H); 
\(^{13}\text{C} \text{NMR (CDCl}_3, \delta\)
–3.8, 13.3, 14.4, 18.4, 25.9, 51.5, 60.3, 124.8, 127.0, 127.7, 129.2, 129.4, 131.7, 133.4, 136.8, 145.9, 150.0, 167.9;
IR (neat) 2949, 2930, 2895, 2858, 1732, 1563, 1452, 1402, 1339, 1294, 1257, 1214, 1169, 1090, 1012, 970, 933, 900, 837, 828, 782, 755 cm\(^{-1}\);
Anal. Calcd for C\textsubscript{23}H\textsubscript{32}O\textsubscript{4}Si: C, 68.96; H, 8.05. Found: C, 69.03; H, 8.01.

Synthesis of benzene 25:
According to the general procedure of 9 (Method A), dienone 24 (36.5 mg, 0.0720 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave 25 (24.0 mg, 70.2\%) as a colorless oil.

\[
\text{OSi-BuMe}_2 \quad \text{CO}_2\text{Me} \\
\text{Ph} \\
\text{OMe}
\]

benzene 25
\(^1\text{H} \text{NMR (CDCl}_3, \delta\)
–0.3 (s, 6H), 0.93 (s, 9H), 2.75–2.86 (m, 4H), 3.26 (s, 3H), 3.45 (s, 3H), 7.19–7.39 (m, 8H), 8.15–8.18 (m, 1H);
\(^{13}\text{C} \text{NMR (CDCl}_3, \delta\)
–4.4, 18.1, 23.1, 25.9, 28.9, 51.5, 60.5, 126.1, 127.2, 127.3, 127.4, 128.5, 128.9, 129.4, 133.1, 133.3, 135.6, 136.5, 138.3, 145.8, 148.9, 167.8;
IR (neat) 2948, 2930, 2857, 1733, 1544, 1499, 1472, 1461, 1444, 1361, 1319, 1303, 1275, 1210, 1176, 1125, 1063, 1032, 1019, 971, 881, 841, 781, 769 cm\(^{-1}\);
Anal. Calcd for C\textsubscript{29}H\textsubscript{34}O\textsubscript{4}Si: C, 73.38; H, 7.22. Found: C, 73.19; H, 7.32.